An Investigation into Particulate Air Pollution in London, at a Site on the Archway Road (A1) London .

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Note

This is the report of a summer study into particulate matter on The Archway Road (the A1) – in North London. Appendix B is the report of the pilot study, which was conducted so that the author could familiarise with the equipment and procedures, required for the main study. Appendix C is the report of a winter study carried out At the same site (01/03/99-28/03/99). This study was submitted as a dissertation for the degree of BSc Environmental Science and Technology. It was considered valuable to have all this material in the one report as it provides evidence of the full scale of work undertaken and gives reference to comparative data.

Abstract

Samples were collected for several fractions of particulate matter (PM) at a roadside site - on The Archway Road (the A1) – in North London over a period of 6 weeks commencing 29/06/1998. Twenty-four hour samples were collected for Total Suspended Particulates (TSP) using a Rotheroe and Mitchell L30 pump. PM_{10}, $PM_{2.5}$, PM_1 fractions were monitored using a Partisol Starnet 2000 system (USEPA standard method for PM_{10}). Twenty-four hour Black Smoke (BS) samples were collected using an eight port BS sampler. Twenty four hour PM_{10} was also collected using a portable AirMetric MiniVol™ PM_{10} monitor for comparison. Data collected for different fractions were analysed and compared. Comparisons were also made for the sub-sets of the data for weekends and weekdays.

The 24-hour PM_{10} samples from both monitors were compared using regression analysis. Comparison of means suggested that the AirMetric readings were 110% higher than the Partisol readings. Both PM_{10} data sets were regressed against Partisol $PM_{2.5}$ data, indicating a 4.7% (& a fixed 2.2 μg error) on the part of the AirMetric monitor. Field controls showed that the AirMetric filter housings produced larger filter weight gains than the Partisol filter housings, this was accepted as being partly fixed error. Partisol data showed a PM_{10}: $PM_{2.5}$: PM_1 ratio of 100:76:62, therefore, the equivalent $PM_{2.5}$: PM_1 ratio was found to be 100:81. All PM_{10} data was found to be below the National Air Quality Standard (NAQS) limit of 50 μg m^{-3} with an average of 21 μg m^{-3}. Both PM_{10} and $PM_{2.5}$ were found to compare well with data from other London roadside sites in terms of trends and concentrations. Rural sites were found to compare less well with consistently lower concentrations.

Twenty-four hour TSP was found to average 23 μg m^{-3}, which was found to be low in comparison to published data. Rush hour data showed elevated average concentrations for both morning (RH_{AM}) and evening (RH_{PM}) samples of 40 μg m^{-3} and 42 μg m^{-3} respectively. Week day RH_{PM} concentrations showed more elevation than week end RH_{PM}, whereas week end RH_{AM} rush hours showed highest levels with the maximum recorded concentration being a week day evening rush hour. Average BS concentrations were found to be 22 μg m^{-3} with slightly higher concentrations being found during weekdays in comparison to week-ends. Regression analysis of all 24 hour data sets showed that BS had very weak relationships with all other fractions, whilst TSP displayed no relationships with other fractions and all PM_x fractions were well corelated. Partisol errors were determined by regressing co-located $PM_{2.5}$ data sets.

1. Introduction

1.1 General Introduction to This Study

This study was undertaken as a collaboration between Middlesex University, Haringey Council and the Simon Woolf Action Group (SWAG). The purpose being to establish the levels of particulate air pollution typical of the Archway Road. The study incorporated the use of a portable PM_{10} monitor (an AirMetric Minivol sampler) which was purchased in memory of a pro-active scientist, Simon Woolf, who supported the efforts of the pressure group during earlier campaigns. This monitor was part funded by the proceeds of local community fund-raising and was part funded by Haringey Council.

The literature review includes information regarding the urban aerosol in terms of composition and physio-chemical characteristics. More specific information regarding vehicle emissions is provided as the study is based beside a busy A-road in an urban area. Some general information as to the health effects, including deposition and clearance mechanisms are provided as the report will be handed on to SWAG and this is one of their concerns. Background information with regards to aerosol measurement is provided in an attempt to put the techniques used into perspective.

The study itself was an investigation of TSP, PM_{10}, $PM_{2.5}$, PM_1 and black smoke concentrations as 24-hour averages and of rush hour concentrations for TSP and PM_{10}. This was undertaken over a six-week period in the summer time and was intended to give some impression of 'typical' summer conditions. For this reason, comparisons were made with other sites and with the same period in previous years. This report aims to provide a perspective on the levels of particulate pollution on the Archway Road.

1.2 Introduction to the Aerosol

Aerosols occur naturally, ever since humankind started to light fires there has been a significant anthroprogenic influence on ambient urban aerosols. As the larger cities developed, and again as the industrial age dawned, coal and wood were burned in large quantities and in more concentrated localities. This resulted in the release of large concentrations of smoke into the urban atmosphere, this in turn had a profound effect on the ambient air quality. The work of the French Impressionist Monet reflects this, when he painted the barely visible Houses of Parliament across the River Thames in the late 19th century. The scene is now interpreted as being an Impressionists' view of London and although this is true, the colour schemes and hazy quality were a direct result of the poor air quality of the times. The aerosols acted as a filter and cutting out the blue part of the spectrum in the evening, enhancing the sunsets (this phenomena still occurs to a lesser degree today). Similar scenes are also reflected in the work of J. W. Turner.

It follows that the problems related to particulate air pollution that we face today are by no means a recent phenomenon. In fact, levels of particulates are now probably lower than they have been for many decades. Our recently acquired ability to perceive the health implications, measure and analyse this aspect of our urban environment has resulted in a recent effort to study and reduce urban aerosol concentrations.

In the following sections, the background to the field of airborne particulates is reviewed. This requires the introduction of several definitions and concepts that standardise the terminology used by the scientific community to discus the field. As in all areas of science, this is of importance, especially in a field where the focus of attention is of an extremely diverse and complex nature. These definitions can be found in Appendix A

1.3 The Human Significance of the Ambient Aerosol

Ambient aerosols are of particular significance as they impact on the life of individuals in a number of ways, including aesthetic effects; effects on the environment (biodiversity); infrastructure damage and health impacts. Consequently, local authorities, national government and international bodies all show an interest in these aerosols.

Arguably, the individual is primarily affected by the health impacts associated with air pollution, either to themselves or to their dependants. Such impacts generally take the form of the aggravation of existing conditions and are, therefore, not entirely obvious to the individual. Another, more immediate impact is the soiling of buildings, which could impact on their value and the costs of their up-keep.

Within the UK, local authorities are now obliged to evaluate the ambient air quality of their borough/district in order to demonstrate compliance with recent regulations (National Air Quality Standard: NAQS 1998). These regulations are intended not only to protect the health of the local population, but also to have an impact on the profile of the city or district itself. Additionally it is intended that they will help reduce the clean up and repair costs that are incurred as a result of particulate air pollution. With respect to the latter, the soiling and damage to public buildings and sites of historical significance have been researched for some time now. In particular, much interest is being shown in calculating and predicting the costs of cleanup with the costs of reducing levels of urban air pollution on an international scale.

At the national level, government is primarily responsible for the health of its citizens, in as much as processes sanctioned by the government should not be detrimental to the health of the general public. The government has the power to enforce the adoption of the best practicable policies and considers the economic impacts of such policies. Such impacts are often complex i.e., the soiling of public historic buildings incur clean-up costs but also depreciates the aesthetic value of major cities. This in turn may affect income from the tourist industry, or even the image (and the commercial performance) of companies operating in degraded buildings. The structural damage to buildings such as St Paul's Cathedral in London could become a serious concern to the Church, the general public and tourists.

At an international level, government can address the issue as a global problem. Evidence has emerged that the ambient air quality in the British Isles is profoundly influenced by the movement of contaminated air masses from the continent over the country (King *et al.*, 1997). Given that the diverse nature of the major source of the modern urban aerosols is traffic, it is possible that ultimate solutions will only be reached through a long slow process of co-operation and investment in alternative systems and policies.

2. CHARACTERISTICS OF AMBIENT AEROSOLS

This chapter examines the nature of ambient aerosols, the primary and secondary sources of these aerosols and their relevant emissions are considered. Particular attention is paid to vehicle related emissions (as this study is located directly beside and above a busy inner city A-road where vehicle emissions would appear to represent a major contribution to the ambient aerosol). Typical distributions in terms of particle size and total particulate mass are briefly discussed.

2.1 Typical Ambient Aerosol Composition

Ambient aerosol is a term used to describe an aerosol that is typical of a given location at a given point in time. Strictly, this not only includes the particulates (solid or liquid), but also the surrounding air that contains them (Wilson and Spengler, 1996). The major distinctions made in the classification of sources are between those of primary and secondary origins (see section 2.3) and between those of natural or anthropogenic origin.

No ambient urban aerosol can be considered as having a typical composition as there are several factors which effect their composition: e.g. atmospheric chemical reactions, contributing local and non-local sources combined with transport effects and removal mechanisms (QUARG 1996). Those particles with smaller aerodynamic diameters have longer airborne residence times (depending on the removal mechanisms in action), therefore these fine particulates tend to have more uniform dispersal patterns over larger areas. For example, fine particulate sulphate (SO_4^{2-}) shows good spatial uniformity across the UK (QUARG 1996). However, a British national survey showed that the mass concentrations for secondary aerosols (tending to be in the fine fraction) displayed a spatial gradient, with the highest concentrations in the South East and lowest in the North West (QUARG 1996). This can be related to long range transportation of continental aerosols (King and Dorling 1997; Brook 1997).

Coarse mode particulates show strong spatial gradients, having larger mass and, therefore, a shorter airborne residence time (i.e. a higher deposition velocity). Dispersal depends entirely on the ambient conditions such as wind speed and rainfall. Examples of coarse mode aerosols are resuspended dusts, soils and sea spray.

This study lacks any meteorological data, which, in the light of the seasonal comparisons being made, is a major short fall. The relevance of this will be discussed in more detail later (see section 2.5).

Common inconsistencies worth considering in the discussion of "typical composition" are:

- Localised sources (especially of coarse mode particulates) i.e. marine spray at coastal sites give increased concentrations of chlorine (Cl^-), sodium (Na^+), magnesium (Mg^{2+}), potassium (K^+) and calcium (Ca^{2+});
- The type of sampler used will affect the size fraction being sampled;
- The choice of species being sampled for as it is currently impossible to analyse for all aerosol components;
- The method of analysis used will limit analysis due to detection limits and interference associated with the method;
- Seasonal, meteorological and source variations produce temporal fluctuations;
- Variations in humidity when sampling will affect the size distribution of the hygroscopic aerosol component (this being especially true for marine aerosols);

To date, our knowledge of ambient aerosols should not be regarded as definitive. This is largely due to most studies having concentrated on the toxic metal and organic compound components of aerosols (QUARG 1996). This has resulted in a lack of detailed information on other aspects of aerosols. Considerations concerning the size range of particulate matter samples are important, as there are distinct changes in the concentrations of some species as a function of size i.e. between the coarse and fine mode particles. One generalisation is that the coarse mode is of natural origin and the fine mode is of anthropogenic origin. It is in fact more true to say that the coarse mode is the result of mechanical processes and that the fine mode is a produced by chemical, hot industrial and other combustion processes.

Table 1 shows some typical values for aerosol composition in the UK. Typically, the coarse fraction contributes around 90% of the total aerosol in terms of mass. Most of the minerals are present in this fraction (elevated levels of Cl^-, Na^+, Mg^{2+}, K^+ and Ca^{2+} are common if there is any sea salt input to the aerosol). The fine fraction will typically show depleted levels of the above and will show a major increase in the levels of combustion and hot process

products such as: elemental carbon (EC), of sulphate ions (SO_4^{2-}), oxides of nitrogen (NO_x) and of ammonium ions (NH_4^+), these generally being of anthropogenic origin.

Table 1 Showing typical values for the composition of ambient aerosols (QUARG 1993).

ANALYTE	TYPICAL CONC.	FRACTION OF TOTAL	IN FINE FRACTION
SOLUBLE IONS:			
SULPHATE	5-10 $\mu g\ m^{-3}$	20-25%	85%
NITRATE	2-10 $\mu g\ m^{-3}$	10-20%	60-70%
CHLORIDE	1-3 $\mu g\ m^{-3}$	<10%	10%
AMMONIUM	2-6 $\mu g\ m^{-3}$	<15%	>95%
STRONG ACID (H^+)	0.02 $\mu g\ m^{-3}$	Trace	100%
CARBONACEOUS:			
PEC	3 $\mu g\ m^{-3}$	10%	80%
OC	5 $\mu g\ m^{-3}$	15%	80%
MINERALS	8 $\mu g\ m^{-3}$	20-25%	5%
METALS:			
Na	1 $\mu g\ m^{-3}$	2%	21%
Mg	0.1 $\mu g\ m^{-3}$	0.20%	19%
Ca	0.4 $\mu g\ m^{-3}$	0.80%	25%
K	0.1 $\mu g\ m^{-3}$	0.20%	44%
Pb	0.1 $\mu g\ m^{-3}$	1%	90%
Fe	0.5 $\mu g\ m^{-3}$	0.50%	35%
TRACE	5-50 $ng\ m^{-3}$	Trace	Most
TOXIC ORGANIC MICROPOLLUTANTS:			
DIOXINS	200 $fg\ m^{-3}$	Trace	Most
PCB's	1 $ng\ m^{-3}$	Trace	Most
PAH	150 $ng\ m^{-3}$	Trace	Most

KEY: **PEC particulate elemental carbon** **OC Organic carbon**
PCB's Polychloylbiphenyls **PAH Polyaromatichydrocarbons**

2.2 Sources and Emissions of Airborne Particulates

Airborne particulate matter can be seen as being the product of two distinct types of source; natural and anthropogenic. However, the sources can also be classified in terms of the method of generation, being either mechanical or chemical. The major natural contributors to airborne particulates in the UK are the suspension of soils and dusts and the suspension of sea salts. Both of these sources produce particles predominantly in the coarse mode and, therefore, tend to be significant only locally to the source, however, they serve to illustrate natural contributions to atmospheric aerosols. Other natural sources are volcanic activity (this can influence the UK as a result of long range transport, King and Dorling 1997), natural fires (contributing to the fine fraction), plant particles and other biological particulates (QUARG, 1996 and UN Economic Commission for Europe, 1979).

Anthropogenic contributions to coarse fraction particulates consist of road dust (resuspended), construction, quarrying, mining industry, agriculture and de-icing salt. These are generally only of local significance as they have a short atmospheric residence time. Anthropogenic contributions to fine fraction particulates consist of vehicle exhausts, fossil fuel combustion, incineration, industry, metals industry, waste treatment and handling and secondary particulates from many gaseous emissions. These produce a more generalised impact as particulates in this fraction are airborne for long periods and disperse widely. They also represent a more significant health threat (see later). Anthropogenic contributions generally outweigh those of natural origin partly as they mainly contribute to the fine fraction (UN Economic Commission for Europe 1979) which remains airborne for longer periods and can undergo long range transportation.

a) **b)**

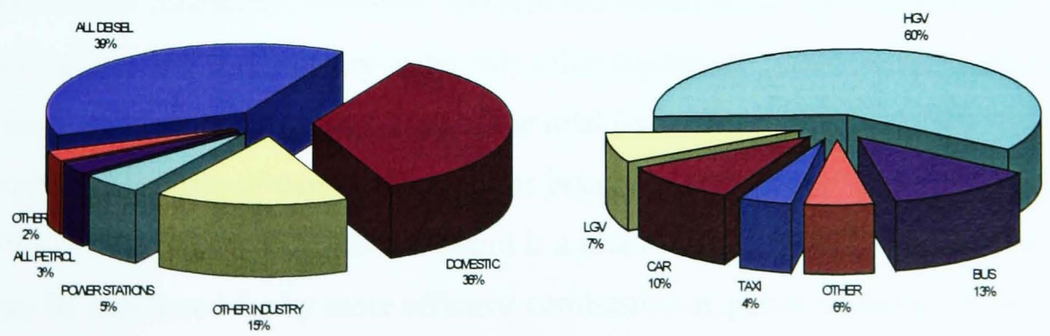


Figure 1: Black smoke emissions inventory (QUARG 1993): a) UK national 1991 b) London .

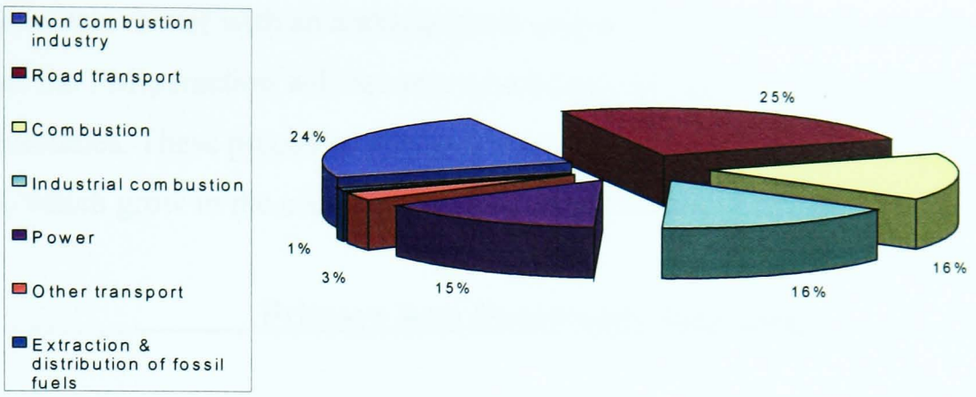


Figure 2: Particulate emissions (anthropogenic) in the UK and their average contribution to total PM_{10} emissions in 1993 (QUARG 1996)

Figure 1 shows the emissions inventory contributing to black smoke (BS, detailed later) in the UK according to QUARG (1993). The main component of the BS is dark, non-reflective, elemental carbon matter with an aerodynamic diameter ≈ 4.0μm (*Pers. comm.* Dr B Gorbunov Middlesex University 1998). This is important in terms of soiling, visual impairment and for health reasons. Originally, during the smogs of the 1950's and 60's, the major source of BS was domestic and industrial coal combustion. Currently in the UK, as shown in Figure 1 (a) the major source in the is diesel combustion (39%) followed by domestic combustion (36%). The domestic aerosol contributions result from the combustion of oil, coal and wood for heating and cooking. Within large urban areas such as London (Figure 1 (b)) diesel emissions have recently dominated the aerosol (84% if all taxis and buses are assumed to be diesel powered). This pattern is true for all major conurbations and serves to highlight the effect of local transport sources on the ambient urban aerosol.

Figure 2 shows the main anthroprogenic sources of particulate matter with an aerodynamic diameter (AD) of less than 10 μm (PM_{10}) emissions in the UK (QUARG 1996). It is clear that combustion (combined industrial and non-industrial) is still the major source of airborne particulates and that industry is the only other significant non-transport source in the UK. Transport contributes around 28% of the total (with diesel making a 70% contribution to that fraction) and 10% of transport emissions being non-exhaust i.e. tyre wear etc. (QUARG 1996). Most reports indicate that petrol is a relatively clean fuel, in terms of particulates (this may be accounted for by more efficient combustion in petrol vehicles). A more detailed account of the processes involved can be found in section 2.7.

As most particulate matter with an anthropogenic origin is found in the fine fraction, it can be accepted that the PM_{10} fraction will become increasingly dominated by hot industrial or combustion sources. These processes generate vapours that condense to form ultra-fine particulates, which grow in the accumulation mode (see section 2.4)

2.3 Primary And Secondary Aerosols.

Primary aerosols are of both anthropogenic and natural origin. The term, primary aerosol, refers to those particulates that remain airborne in the same form as the original emission. The residence time of primary particulates in the atmosphere is dependent on not only size and mass of the particles, but also on their reactivity and the ambient conditions. The urban environment has a large enough number of anthropogenic sources to generate a specific type of ambient aerosol, this is a precursor to secondary particulate production under the right conditions.

In contrast, secondary aerosols result from gas-to-particle conversion processes (Wilson and Spengler 1996). Secondary aerosol formation results in the production of new particulates in the atmosphere, as a consequence of the condensation of hot vapours. These include reactions between gases and existing particulates, and changes in the speciation of interacting particulates and gases (i.e. the conversion of SO^{2-} to H_2SO_4 by oxidation). These can result in photochemical smog pollution events when they are associated with high levels of ozone (O_3). One common conversion process is of SO_2 to particulate sulphates such as ammonium sulphate: $(NH_4)_2SO_4$; another is the formation of particulate nitrates from NOx to form ammonium nitrate: NH_4NH_3 (Chan, 1997).

2.4 Size Distribution

Particulates typically show a tri-modal size distribution when plotted as mass or volume versus aerodynamic diameter (UN Economic Commission for Europe, 1979). With one mode in the 0.0-80 nm AD range, a second in the 80nm-1.5 μm AD range and third in the 1.5- 100 μm AD range. This modal size distribution is the result of the combination of three distinct fractions or modes: the nucleation mode also termed the Aitken nuclei range, the accumulation mode and the coarse mode (Figure 3).

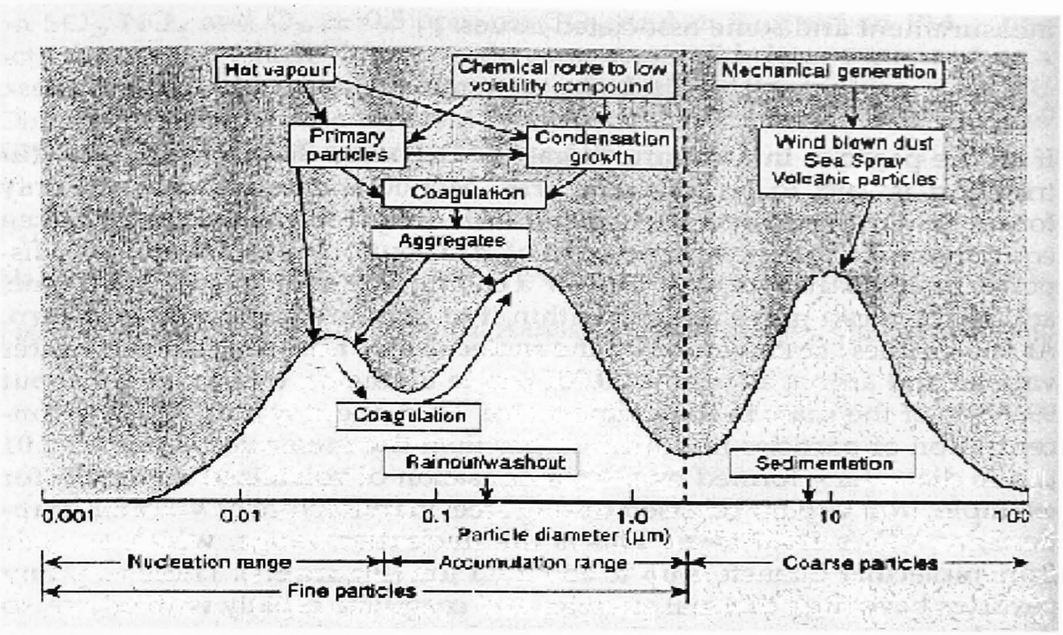


Figure 3: Schematic showing the modal distribution of airborne particulates, their origins and removal mechanisms (source: Wilson and Spengler 1996).

2.4.1 The Nucleation Mode

This mode results from the direct condensation of non-volatile material. Either being vaporised from a hot surface such as an exhaust, some industrial process, or has occurred as a result of gas-phase reactions in the atmosphere forming non-volatile material (i.e. the conversion of SO_2 to H_2SO_4 by oxidation). This process involves the introduction of similar molecules to each other when they exist as a vapour in concentrations exceeding the vapour pressure of the substance (at atmospheric temperature and pressure). Minute particles are formed which act as condensation nuclei for other similar molecules. This process is self-limiting in terms of numbers as once a certain concentration of nuclei are present, they are more likely to grow than new nuclei are to form (QUARG 1996).

Particles in the nucleation mode are very light and fine with ADs typically less than 80nm and commonly around 0.02 nm (QUARG 1996, Wilson and Spengler (1996), USEPA (1996), UN Economic Commission for Europe (1979)). They tend to be generated in large numbers (Wilson and Spengler 1996), often as smoke or fume, going on to form particles in the accumulation mode through both accumulation and gas particle reactions (formation of secondary particulates).

2.4.2 The Accumulation Mode

This mode results from the accumulation of more than one type of non-volatile onto the existing condensation nuclei. Much the same process occurs as with the nucleation mode, except that the existing nuclei offer a larger surface area for condensation to occur. In addition, existing nuclei can offer reaction sites for reactions such as the oxidation of SO_2 to H_2SO_4 and so grow in size.

Typically accumulation mode particles exist in the size range 0.05 to 2.0 μm AD (QUARG 1996). Consequently, they undergo rapid Brownian motion and agglomerate to form larger particles or denditric chains common to smoke. Particles in this range do not grow into the coarse mode size range, except in the case of cloud formation (*Pers. comm.* Dr B Gorbanov Middlesex University 1998).

2.4.3 The Coarse Mode

This mode exists independently of the accumulation and nucleation modes. The particulates in this mode tend to be natural in source and are generally generated mechanically e.g. volcanic dusts, resuspended dust and soils and sea spray, but includes some biological particles which tend to be seasonal e.g. pollen, fungal spores etc.

The division between the fine and coarse modes lies in the size range spanning 1.0 to 3.0 μm diameter generally being reported as 2.0 μm (UN Economic Commission for Europe 1979). The extent of this mode is not only dependent on the local sources but also on ambient conditions i.e. there will be a greater influence from sea spray and resuspended dusts/soil in hot dry conditions. The prospect of such particles remaining airborne decreases with size due to their increasing deposition velocity and, therefore, sources are commonly localised.

2.5 Meteorological influences

Weather has a subtle effect on particulate concentrations, this being due to the inability to separate the effects of one aspect from another. Large weather systems can have significant

effects on a countrywide basis, with time lags as small as a few hours or less. Large weather systems from Europe may carry continental particulates into the UK (King A et al 1997 and Steadman 1996).

Particulate concentrations generally correlate well with sunshine. This is partly due to the fact that the main sources of particulates are of anthroprogenical origin and the local sources are emitted during daylight hours when people are more active. There is also the effect of sunshine during the summer when elevated temperatures and light stimulate the production of secondary particulates (QUARG 1996).

Summer smog events are associated with anticyclonic conditions, light winds, high temperatures and clear skies (or strong sunlight). Winter smog events are associated with anticyclonic conditions, low to light wind speeds, low temperatures and shallow mixing depths. The common factors in both cases are poor mixing and dilution of pollutants and a weather system that allows concentrations to collect.

Temperature effects are best considered in terms of winter and summer events. During winter periods there tends to be an inverse relationship between temperature and particulate concentration. This is largely due to the increased use of fuels for heat and the effects of cold starts and reduced engine efficiencies. The summer time trend is reversed showing a dependant relationship, this is often due to the build up of traffic related sources coupled with increased secondary production as the day progresses.

During the winter, the wind tends to have a dilution and dispersion effect, reducing the ambient concentrations through dilution of local emissions. This can be said as the winter rains and precipitations tend to result in the suppression of deposited particulate matter and inhibit re-suspension. Summer winds however can reverse the winter trends, re-suspension of street and road dusts, soils, construction dust and sea salt aerosols all contribute to PM10 levels and especially TSP in the absence of precipitation.

2.6 Airborne Residence Times

It is the physical characteristics that determine the time that atmospheric particulates remain airborne. In general, particulates of 0.1-2.0 μm AD will remain airborne for long periods and can be transported over longer distances. The >2.0 μm diameter range will tend to be deposited more rapidly as a result of gravity. Very fine particles i.e. those with a diameter of < 0.1 μm tend to agglomerate or act as condensation nuclei and are either washed out or take part in secondary particulate formation. The overall size range of particulates is restricted at the lower end by the size of the smallest condensation nucleus (i.e. a few nm or at least several molecules) and at the larger end to the size of a grain of sand (around 200-2000 μm). The latter can only remain airborne for short periods (depending on the wind speed).

2.7 Vehicle Related Emissions

In 1973 Habibi wrote, "Although, on the basis of mass, the contribution of vehicle particulate emissions to total atmospheric particulate loading is small, their effect on ambient air quality may be more significant". However, in 1995 a study was set up comparing the PM_{10} concentrations at two urban sites and one rural site (Cardiff, Bristol and Chew Valley Lake respectively), using TEOM instruments over the period 24th January to 21st February. Results showed the mean concentration of PM_{10} (from hourly averages) to be 20 μg m^{-3}, 23 μg m^{-3} and 14 μg m^{-3} respectively (QUARG 1996) – Urban/rural varriation being attributed to vehicle pollution.

Ter Haal *et al* (1972) showed that vehicle emissions vary widely from vehicle to vehicle, Habibi (1973) and Ganley and Springer (1974) agreed that the emissions depended on a great many factors. Fuel type was of concern at the time as the potential detrimental health effects of lead (Pb) salts in the air and road dusts had been realised and alternatives were being considered. Habibi showed how lead salts could be responsible for major portions of particulate emissions in certain circumstances. However, Pb was generally associated with particulates of diameters less than 5 μm and less than 5% were in the size range below 1 μm diameter. In general, both parties (Habibi 1973; Ganley and Springer 1974) agreed that around 30% of particulate emissions from leaded petrol would be lead associated.

Unleaded fuel showed trace levels of Pb, probably coming from the engine oil and possibly from contamination during handling by the producers. With unleaded petrol the carbon emissions are greatly increased (Habibi 1973; Ganley and Springer 1974) 35% of emissions from leaded petrol consisted of carbonaceous material whereas for unleaded petrol the figure is around 70% (Ter Haal *et al* 1972). Habibi wrote in 1973 "If unleaded petrol emissions do not reduce or eliminate carbonaceous particulates in vehicle exhausts then the mechanisms should be examined and their formation controlled". This is particularly relevant to today's urban aerosol as particulate elemental carbon (PEC) is an irritant and can carry volatile organic compounds (VOC's) which are in some cases known to be toxic and/or carcinogenic.

All the above recognised that several factors effect the actual emissions from a given vehicle. The running temperature of the engine effects the efficiency of combustion. Engine speed effects the velocities of particulates in the exhaust system and therefore their deposition and/or re-entrainment. Exhaust length and design effect internal turbulence and deposition. The type of driving, town or main roads (stop start or continuous) the fuel type, consumption, loading and age of vehicle are all of importance. Cold starts alone increase PM emissions by two to eight times (Ter Haal *et al* 1972).

Particulate vehicle emissions were shown to contain Pb, P, S, C, Fe, Br and other trace elements as well as a range of organic compounds (Ter Haal et al 1972). Engine emissions were found to be mainly in the < 1.0 μm range, coarse particles being generally > 5.0 μm in diameter with a negligible contribution from the 0.5-5.0 μm range (Ter Haal et al 1972). The smaller particles are invariably spherical, being of secondary origin, the larger particles are mostly amorphous, resulting from coagulation or build-up and re-entrainment (Ter Haal et al 1972).

3. HEALTH EFFECTS OF AEROSOLS

The health implications associated with the inhalation of urban aerosols have long been recognised if not fully understood. Excess mortality has been shown to be associated with elevated levels of particulate air pollution. As a direct result of this, research has taken place into the health effects of urban aerosols around the world. In the United Kingdom, this body of work has been reviewed by the Committee on the Medical Effects of Air Pollutants (COMEAP) (1996) and condensed into one document. This has served to provide the decision-makers with some basis for decision making and action. Other major documents on the nature of particulates and on air quality and its implications produced for government include the Quality of Urban Air Review Group reports (QUARG 1993(a), 1993(b) and 1996) and the work of the Expert Panel on Air Quality (EPAQS).

Within this chapter, the basic principles of particulate deposition in the lung are reviewed, as are considerations with respect to human dosimetry and the health impacts of particulates in urban areas.

3.1 General Background

Studies of London studies in the 1950's and 1960's showed a highly significant correlation between the famous smog events and excess mortality (see Figure 4). This was the first occasion where a firm link was drawn between particulate pollution and excess deaths. However, at the time the pollution was not restricted to particulates (BS method) but also sulphur dioxide (SO_2) The pH of the smogs was reported as being around 1.6 during this period (Brimblecombe 1987). This led to the conclusion that most excess deaths were attributable to the acid aerosol, with reports of lung impairment by the induced production of large quantities of mucus.

Since then, a large number of epidemiological studies have assessed the relationship between excess mortality and particulate pollution levels. These studies appear to show that there is a definite effect at current ambient levels. This effect is larger than would be expected if simply extrapolated from early studies (COMEAP, 1996) and therefore may reflect the changing

nature of the particulate matter or the nature of air pollution in general (see Figure 5). Alternatively, this may be a reflection of the non-linear dose-response curve attributed to particulate air pollution.

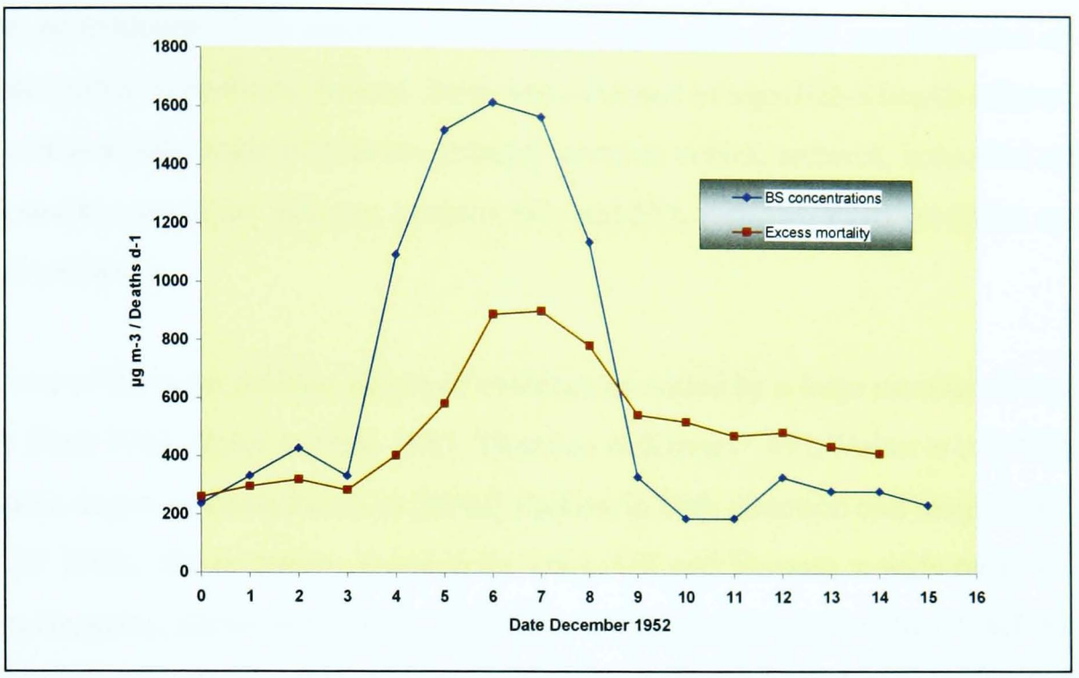


Figure 4: The London smog event 1952 and excess deaths over the same period (source Brimblecombe 1987)

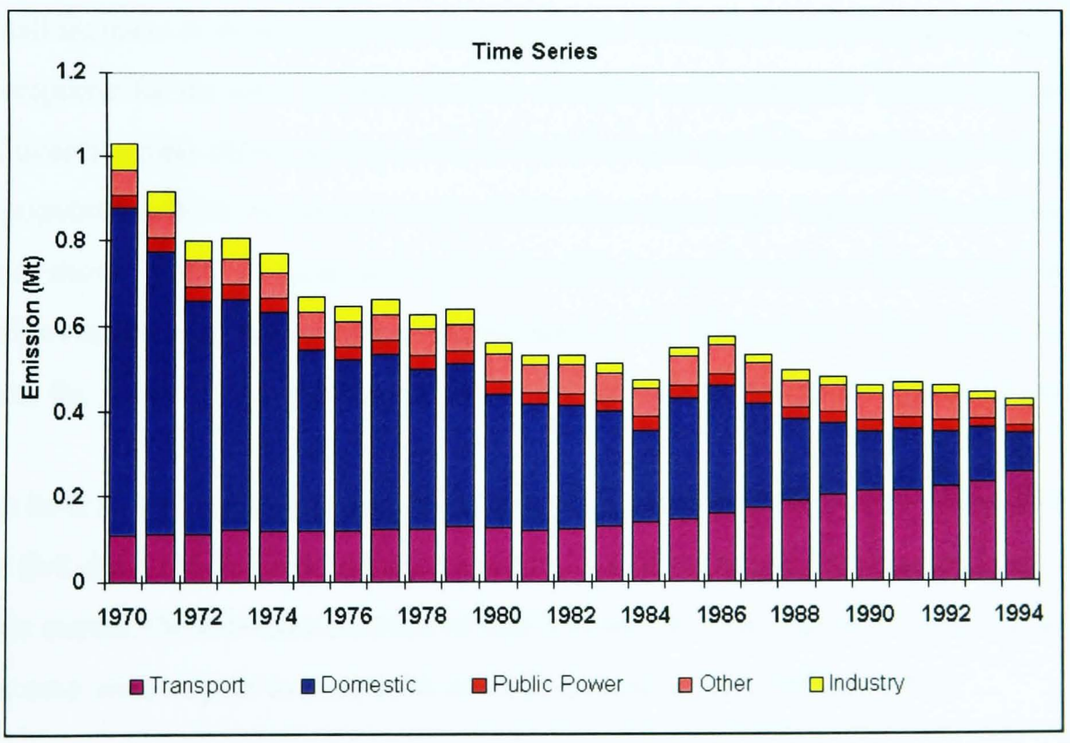


Figure 5: The changing nature of particulate emissions (as black smoke) showing rise in transport contributions 1970-1994. (Source www.aeat.co.uk/netcen/airqual/emissions/bsbar.gif)

The evidence, as reviewed by COMEAP (1996), indicates associations between particulate concentrations in ambient air and changes in lung function, increased symptoms of existing health conditions, days of restricted activity, increases in hospital admissions and mortality. However, no evidence of any associations between health effects and specific types of particulate matter were found. Indeed, there was evidence of significant health effects resulting from a wide range of sources: primary sources: vehicle exhaust, industrial emissions and coal smoke; secondary sources: gaseous SO_2 and NO_x resulting from vehicular and industrial emissions.

Perhaps one of the most striking pieces of evidence provided by a large number of studies (Bates & Sizto 1983, Bates & Sizto 1987, Thurston & Kinney 1992,Walter *et al* 1994) is the "remarkable degree of consistency in [these] studies, in both direction and magnitude" (COMEAP 1996). These studies, based in the USA, UK and Toronto, a wide range of other studies in Germany, China and Greece, (EPAQS, 1995) were considered by COMEAP. With respect to mortality, this consistency indicated no threshold dose level, below which there would be a zero effect of particulate inhalation. Rather an initial linear response between dose and response is followed by a shoulder and a diminished curvilinear response. This suggests that a small increase in dose results in a large increase in response at low concentrations and a smaller response for the same increase in dose at higher concentrations. This is explained in terms of quantitatively different responses in sensitive and resistant populations within the general population. With the sensitive population showing a high response the resistant population showing the later response as concentrations continue to rise (commonly referred to as the harvest theory). If harvesting is confirmed it is of obvious relevance to the setting of guidelines, the framing of legislation and to the development of monitoring programmes.

Although both COMEAP (1996) and EPAQS (1998) report that there is no conclusive evidence that the responses observed are causally linked to the ambient concentrations of particulate matter, these bodies considered that it would be "imprudent not to consider this as being the case with respect to the health of British citizens" (COMEAP 1996).

Some of the general findings of the above reports to be discussed further are:

- Particulates have a non-specific action, although, individual species can, and do have specific effects (COMEAP 1996).
- The high-risk population are the elderly, the very young and the chronically ill (chronically ill generally refers to sufferers of pre-existing respiratory or cardio-vascular illness).
- Certain acute conditions are aggravated by particulate matter, most conspicuously, respiratory infections, asthma and cardiac arrest.
- There is no evidence to show that there is any effect on healthy people at current UK ambient levels.
- PM_{10} is considered a suitable size range to monitor as it represents the thoracic and respirable fraction of the ambient aerosol.
- Ultrafines (<0.05 μm AD) have been associated with inflammatory response in animals.
- The response to particulates is generally inversely proportional to the aerodynamic diameter.
- Links have been established with pollutant mixtures (BS & SO_2) for many years.

3.2 Deposition Mechanisms

There are five recognised physical deposition mechanisms for particulates. All but one of these has a role to play in the deposition patterns of particulates observed in the respiratory system. These are; impaction, sedimentation, diffusion, interception and electrostatic precipitation (the latter being irrelevant in the lung).

Impaction depends upon the mass (volume and density) and velocity of a given particle i.e. its momentum. A particle has a given inertia in an air flow (an inhaled breath), this denotes ability to move with the airflow through changes in direction (i.e. at the back of the nose and throat, or at bifurcations in bronchioles). If the particle has a high momentum it may be unable to change direction with the airflow and therefore is likely to become impacted on the airway walls. This process results in a very high probability of deposition for particles with an AD > 1.0 μm in the nasopharangeal region and upper airways (the trachea and bronchioles).

This process is enhanced by the vortices produced at the bifurcations and ribbing of the trachea and bronchioli. Bronchial dimensions also affect this process, changes in dimension result in different flow rates, increased velocity results in increased impaction. The dimensions of the bronchioles are dependent on age, physique and gender. Women tend to have a 1.5 cm diameter trachea where men tend to have 2.0 cm diameter trachea (see Figure 7). Consequently, air stream velocities may be higher in the female respiratory system resulting in enhanced deposition by impaction. In contrast to large particles, ultra-fine particles do not deposit by impaction as they lack the momentum to penetrate the micro-layer of still air (boundary layer) which is known to overlie all surfaces (*Pers. Comm.* Prof. Priest Middlesex University 1999).

Sedimentation results from the effects of gravity on particles and occurs as a result of low flow rates; as the flow rates decrease the heavier particles start to fall out of the air stream. This becomes important in the bronchioles where low flow rates can occur. As the terminal settling velocity of a particle is dependent on the square of its diameter, this process is less efficient than impaction and becomes prominent in the region of AD 0.5<1.0 μm particles.

Diffusion occurs as a result of Brownian motion, the process describing the paths of very fine particulates, which are effected by collisions with molecules, and other particulates. The fact that they don't travel in straight lines increases the likelihood of their becoming impacted on surrounding surfaces. This process is important for ultrafines in the nasopharyngeal region (*Pers. comm.,* Prof. N. Priest Middlesex University 1998) and for particles < 0.1 μm AD in the alveolar region of the lungs.

Interception is a special case of impaction and occurs when particles are deposited as a result of a change of surface topology (i.e. ribbing in the airway walls). The particle cannot respond as quickly as the airflow as a result of the particle's inertia or simply catches on a surface feature due to the physical dimension of the particulate. This process is particularly relevant to fibres and other irregularly shaped particles that commonly deposit around bifurcations in the airways.

Electrostatic precipitation occurs as a result of charged particles being attracted to surfaces carrying the opposite charge. Where the charged fibres of a filter cause a deflection in the

flight path of a particle which carries the same charge or where charged particulates are attracted to earth (*Pers. comm.* Dr B. Gorbunov Middlesex University 1998). However, as most ambient particulate pollution is neutralised by the ions in the atmosphere, this process is of no relevance to the deposition of particulates in the lung. Such a process is of relevance to specific conditions and industrial processes, provides the mechanism for the operation of electrostatic precipitators, and may interfere in the deposition of particulates in instruments such as the cascade impactor. This may also be relevant in sampling systems where non-collecting surfaces become charged as a result of friction.

3.3 Non-Ideal Behaviour of Particles

The deposition of roughly spherical particulate matter is governed by simple rules. However, non-spherical particles can behave differently, for example fibres tend to align with the airflow and consequently penetrate deeper into the lung than an equivalent diameter sphere. Fibres of up to 350 μm in length have been found in the alveoli (COMEAP 1996).

Solubility and humidity will effect a particle's size; hydrophilic particles such as those comprising of NaCl have shown growth of up to 4.5 times. Therefore relative humidity will have a pronounced effect on the uptake of these species, this is of particular importance to aerosol scientists and is discussed in more detail in section 4.4.

3.4 Clearance Mechanisms

3.4.1 Nasal Hair and Mucus

The nasal cavity is protected by the presence of nasal hair and mucus. Most of the particulate material > 10.0 μm is removed in this area along with a large proportion of the ultrafine fraction. Part of this is due to filtration in the nasal hair and also by impaction and through diffusion (for ultrafine particulates) onto the mucus membrane lining the cavity. This mucus is then cleared to the throat and stomach.

3.4.2 The Mucocilliary Escalator

In the upper airways, the bronchi are lined with a fine coating of hairs known as cilia. The bronchiolar walls are also covered in a mucus layer, which helps to trap particles deposited there. The cilia beat at a high frequency with the result that trapped material is slowly moved up the airway to the larynx. Here the mucus is either swallowed or cleared from the throat by spitting. Clearance by this process typically takes around 24 hours, but is slower in heavy smokers where many ciliated cells can be missing.

3.4.3 Macrophages and Phagocytosis

The unciliated and terminal alveoli of the lung contain scavenger cells; the macrophages. These cells are similar to the white blood cells in that they ingest foreign particles by the process of phagocytosis. Any particles that the macrophages are unable to ingest are coated by a proteinacous material (i.e. asbestos fibres that penetrate to the deep lung). Materials contained within the macrophage slowly dissolve and their components are returned to the bloodstream. This process can take many years for "insoluble" particles and during this time they may be transferred between several cells. In addition, some particles may remain free in the alveolar spaces, these will also dissolve slowly. Finally, some material in macrophages may become translocated with the phage to regional lymph nodes or to the stomach - if the cell migrates onto the mucocilliary escalator.

Clearance by this method is generally regarded to be a slow process, it can take several years and is dependent on the chemical properties of the particle (COMEAP 1996). In contrast, a recent study using 1.2 μm aluminium oxide particles (highly insoluble) indicated a slow mechanical clearance time of around 86 days for this process (*Pers. comm.* Unpublished data, Prof. Priest, Middlesex University 1999).

3.5 Factors Effecting Human Deposition

3.5.1 Breathing Types and Cycles

There are three recognised modes of breathing; nasal, oronasal and oral. Each of these types will influence the extent and pattern of lung deposition that occurs after the inhalation of a given aerosol concentration.

Nasal breathing is the most common method of breathing in a relaxed, healthy individual. This method has several advantages, it results in the efficient filtering of 90% of larger particles from the air stream (COMEAP 1996), allows for the deposition of ultrafines in the nasal cavity and gives time to effectively precondition inhaled air to body temperature and humidity conditions.

Nasal breathing does not remain equal between left and right nostrils. Rather it tends to cycle between approximately 20% airflow via the left nostril/80% airflow via the right nostril and 80% airflow via the left nostril/20% airflow via the right nostril. This is thought to create more turbulent flows within the nasal cavity and therefore increase the deposition in this area, although the effect diminishes with age, exercise, and disease (COMEAP 1996).

Oronasal breathing is effective at filtering the larger particles from the air stream if the intake of breath is taken through the nose. When the intake is taken through the mouth this effect is diminished. Intake of breath via the mouth results in the impaction of larger particles on the back of the throat. Oronasal breathing increases with exercise (COMEAP 1996) allowing for quicker deeper breaths to be taken due to reduced airway restriction.

Oral breathing is the least effective method for removing particulate matter. This method results in greater deposition in the larynx and a greater percentage of total suspended particulates penetrating to the lungs (COMEAP 1996). This type of breathing dominates during heavy excersise.

3.5.2 Lifestyle

The impact of lifestyle on the number of particles deposited in the respiratory tract of an individual (dose) is important. Lifestyle factors that have been found to result changes of dose include:

Time spent indoors;

Time spent socialising;

Amount of exercise taken (including type and location of exercise);

Place and nature of work;

Smoking;

Presence/absence of specific allergens;

In respect to the above, it has been shown that the major sources of exposure to particulate pollution is smoking and social gatherings where smoking is prevalent i.e. particularly in public houses, cafes and restaurants. Examples of varying levels of exposure to particulate pollution in different environments are shown in Figure 6.

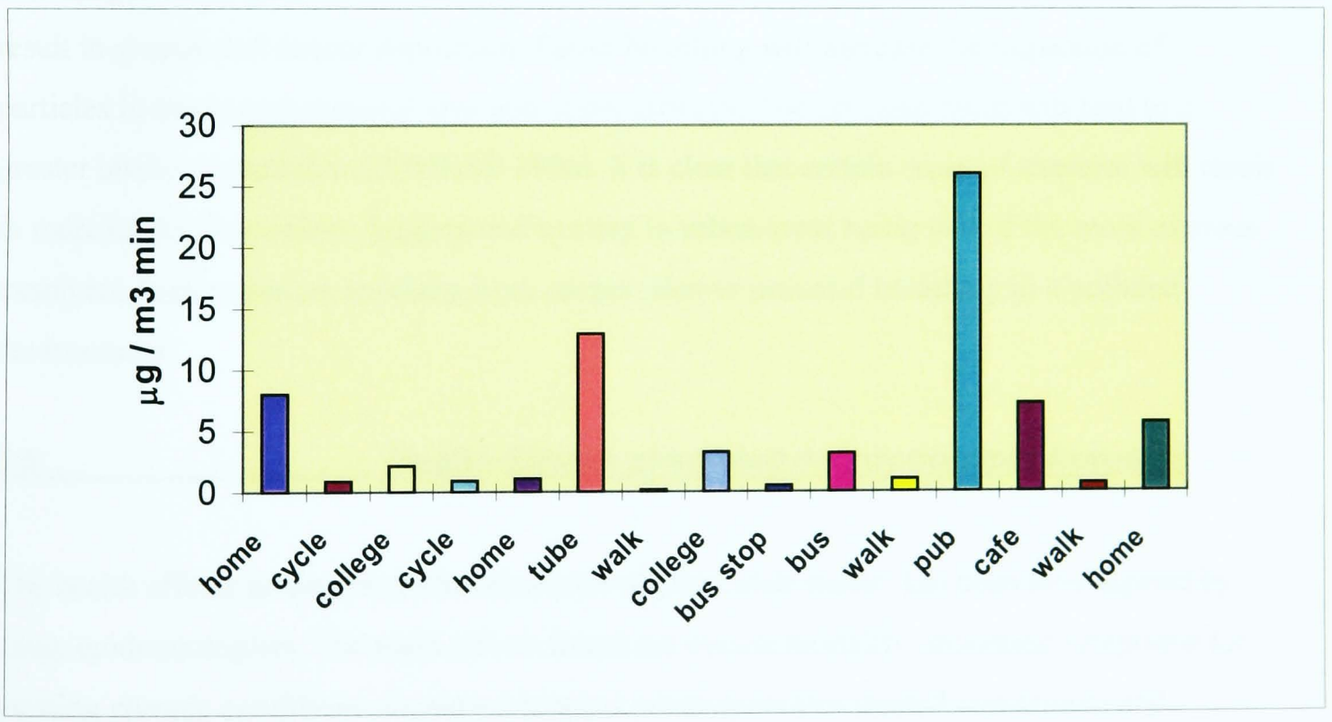


Figure 6: The relative contributions to total 24-hour personal exposure to PM_{10} by micro-environment, for a student living in London. (*Pers. Comm.* Prof. Priest, Unpublished data, Middlesex University 1999)

Indoor air pollution is of great concern, as not only does the average house provides several sources of particulate air pollution (e.g. cooking, heating, moulds/fungal spores and house dust mites). Moreover, many houses are well sealed, causing a build-up of pollutants within the indoor atmosphere. In addition, it is known that submicron particles penetrate indoors, from external sources. There is evidence of increased toxicity of particles when animals are exposed to the same species with AD =20 nm (COMEAP 1996).

The place and type of work is also important to the exposure pattern of adults to particulates. Particularly where the work is of a strenuous nature (effecting the breathing mode and cycle) and outdoors in dense urban conurbations, or where the work is associated with a typically dusty industry (i.e. miners). Here the ambient levels tend to be at their highest and the work causes more and possibly deeper oronasal breathing which leads to a greater intake of particulates. In this scenario, it is more than worth considering the effects of long term exposure.

Exercise is relevant as the individual will respond to exertion by increasing the depth of breathing and the oronasal cycle will increase with activity. Slower and deeper breaths will result in greater and deeper deposition. Faster breathing will increase the impaction of particles in the nasopharangeal area and upper airways. The oronasal cycle will lead to a greater intake of particles (COMEAP 1996). It is clear that certain types of exercise will result in more intake than others, jogging and cycling in urban areas being two of the more obvious examples, high exposure resulting from deeper, slower oronasal breathing in a polluted environment.

3.6 Health Effects of Inhaled Anthropogenic Aerosols

The health effects arising from the inhalation of particulate matter has been investigated by many epidemiologists. The main effects found are excess mortality, increased symptoms for existing chronic conditions, increased hospital admissions (for related conditions) and increased numbers of days of restricted activity (DRA's) within exposed populations. To date, most of these effects have been inferred from the results of geographical epidemiological studies where effects within a population have been correlated with ambient air pollution data. It follows that the lack of correlation between dose and effect dictates that the results be

treated with caution. However, the high degree of agreement between geographically diverse studies indicates a definite link between suspended particulate matter (SPM), health effects and excess mortality that are both statistically significant and appear to have no dose threshold (COMEAP 1996).

For example, studies of the 1950's to 1970's London smog events (Brimblecombe 1987) showed a strong correlation between BS and excess daily mortality (see Figure 4). However, a similar, and perhaps more significant, correlation was found for atmospheric pH (atmospheric pH values of 1.6 were recorded). Consequently, controversy remains as to the causation of the excess mortalities. Nevertheless, present day studies have shown highly significant correlations between both PM_{10} and particulate matter with a mean AD of 2.5 μm ($PM_{2.5}$), and mortality. In contrast, in these studies acid data (SO_2 and H^+) did not show significant correlation to mortality, this can be attributed to the much higher atmospheric pH values typical of the present. These values reflect the changes in particulate sources, or more specifically, the decline of the use of coal as a domestic and industrial fuel and, therefore, a decline in the related SO_2 levels (from FeS_2). The present-day correlation with PM_{10} is generally due to the presence of sulphides in oil-based fuels and any local coal based sources.

Generally, most studies reviewed by COMEAP (1996) seem to agree that the order of significance of correlation between particulate matter and health is Fine Particulates (FP) > PM_{10}> total suspended particulate (TSP). The increased effects of FP are biologically more plausible and seem to be well supported by epidemiological studies (COMEAP 1996).

A study conducted in Toronto (Bates & Sizto 1987) showed correlations between mortality and the following (in order of significance): H+ > SO_4 > FP > PM_{10} > TSP (COMEAP 1996). This again shows how the immediate sources determine the specific nature of the local ambient SPM. However, similar studies in Buffalo and New York (Bates and Sizto 1987; 1989), investigating the effects of combinations of particulates and other pollutants, have shown that there is a relationship between O_3 and H^+ exposure (COMEAP 1996). Consequently, ozone (which is also toxic) may have been a confounding factor in the Toronto study.

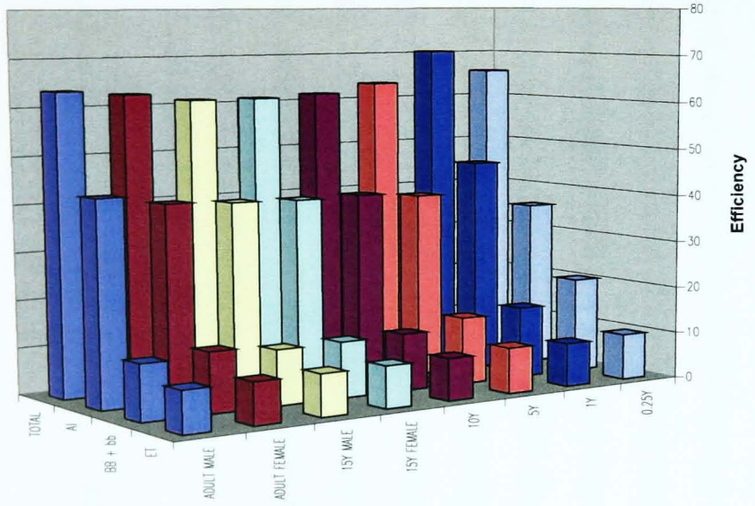
Dose response curves show an increased response at lower particulate concentrations, with larger mortality rates, per unit increase in dose, than at higher concentrations. Although there are some suggestions that a threshold may exist at around 10-15μg m^{-3}, it is claimed that analysis isn't powerful enough to examine dose-response relationships at such low exposures. Alternatively, it has been suggested that the fall-off in mortality at higher concentrations could be due to systematic errors in the measurement of PM at higher concentrations. In addition, it is suggested that BS is a surrogate for some other pollutant (i.e. there is a confounding factor), that days of high exposure may illicit some defensive response or, that the vulnerable population is eliminated in the build up period and, therefore, the response is that of a "selected" more healthy population (i.e. the harvest effect) (COMEAP 1996).

Despite the above, there is clear and irrefutable evidence that those at particular risk are the elderly (>65 yrs), the very young (0-1 yrs) and those suffering from respiratory disease, asthma, chronic obstructive pulmonary disease (COPD). Figure 7 shows that the greatest numbers of particulates <0.5 μm AD are deposited in the alveoli and that there is a marked increase in the efficiency of deposition for persons under 10 years of age.

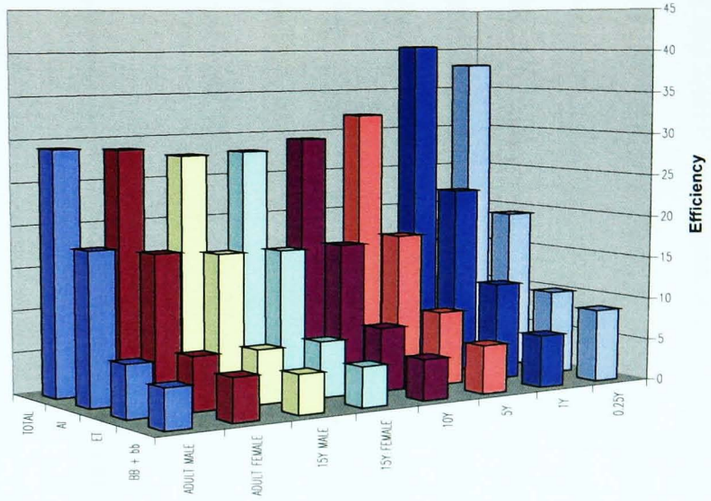
Figure 7: Deposition of various particle sizes in the lung according to region, age and gender **(Source COMEAP 1996)**

ET = extra thoracic AI = Alveolar BB Larger Bronchioli bb = Smaller Bronchioli

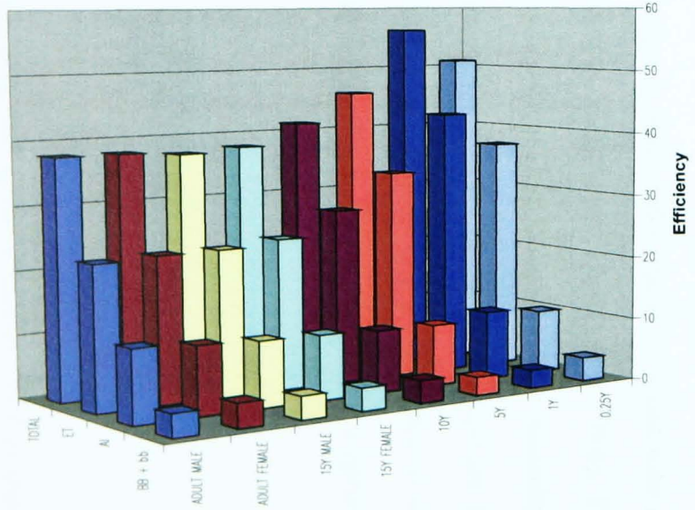
A) 0.05 µm AD



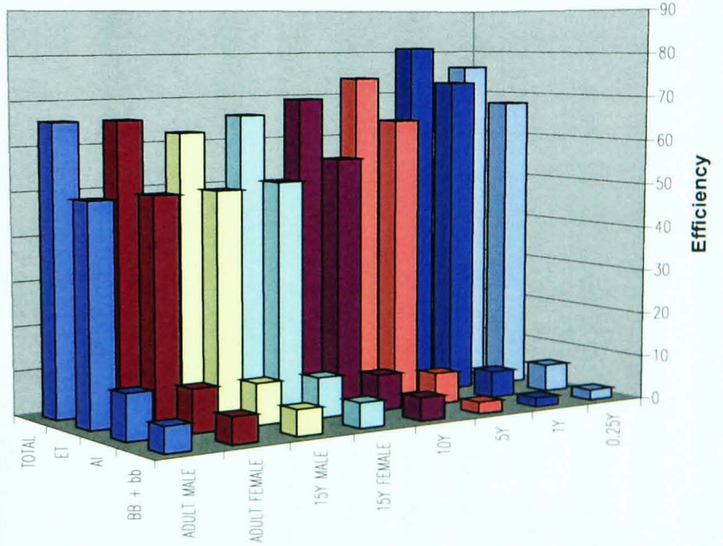
B) 0.2 µm AD



C) 0.7 µm AD



D) 2.0 µm AD



4. MEASUREMENT OF AEROSOL CONCENTRATION

As a result of the health implications, the damage and soiling of buildings and the public nuisance effects of ambient aerosols, their monitoring within urban environments has become common practice. The initial requirement became clear as the air of London clouded over in the 1950's and 1960's and the BS method was first applied (see below). The result was the first correlation between particulate levels and deaths in London during the Fifties (Brimblecombe 1987). In this chapter, the general principles employed in the sampling of aerosols will be considered and the more common and some of the older methods of monitoring will be explained in general terms. Variations in sampler efficiency and some of their causes, the effects of relative humidity and the results of several studies from around the world and in this country are considered.

4.1 Common Measures and Units

In order to avoid any confusion as a result of the ambiguous reporting of results, one of the most important considerations is to be able to agree on the sizing of particulates. Sizing can be a measure of the actual (physical) size of a given particle, if it is measured using a light scattering or similar system (in 'real' time) or by electron microscopy (giving delayed results). Alternatively, the sizing can be considered as a function of its size and mass. The deposition velocity of a given particle (and therefore its atmospheric residence time) is a function of its gross size and density or mass/size ratio (or shape and fractal dimensions, *Pers. comm.* Dr. B. Gorbunov, Middlesex University 1998). The scientific community commonly uses the convention of Aerodynamic Diameter (AD) to describe the size of any given particle being relevant to both common measurement methods (see Equation 3). This is defined for any particle as: a sphere of density ρo (where ρo = 1×10^3 kg m^{-3} i.e. that of water) which has the same terminal settling velocity as the particle in question. For example for a spherical particle of diameter D_1 and density ρ_1:

$$\mathbf{AD} = \mathbf{D}_1(\rho_1/\rho_0)^{1/2} \quad \text{Or.....} \quad \mathbf{AD} = \mathbf{D}_1\sqrt{\rho_1/\rho_0} \quad \text{...Equation 3}$$

Particles with an AD <0.5 μm can be classified using the particle diffusion diameter (PDD) although this is used within environmental science. The particle diffusion diameter is equivalent to that of a

sphere, with the same diffusion coefficient as the particle in question. (*Pers. comm.*: Ms M Kendal). AD and PDD are of little use in terms of describing an aerosol as they give no information concerning size distribution. For the purpose of air pollution monitoring the term PM_x has been employed. This has been useful as the fraction being monitored can be termed as being anything less than its upper limit, despite the details of its distribution. Therefore, an aerosol fraction less than 10 μm in AD would be termed PM_{10} (see below).

In the case of purposely generated aerosols (in industry), the more common convention is to describe the size range around which the aerosol is centred. Mass Median Aerodynamic Diameter (MMAD) is a term which can describe an aerosol, where half the mass is greater in AD than the MMAD and half the mass is lower in AD than the MMAD. Other terms such as the Mass Mean Aerodynamic Diameter may be employed in some situations. This terminology may be more relevant in describing mechanically generated aerosols in situations such as paint shops where the aerosol is desired to be within a given size distribution and centred on an ideal size.

Terms that describe the fraction of an aerosol (generally isolated as a result of monitoring) are defined by the nature of the method of measurement. Some of the more common terms are described in Appendix A. However, it would seem relevant to consider the following before entering into any consideration of published data. PM_{10}, $PM_{2.5}$ and PM_1 refer to Particulate Matter (PM) with a AD less than or equal to the size indicated by the subscript. For example the class PM_{10} indicates particulate matter with a AD ≤10 μm. In practice the cut off point of a mechanical sampler which collects onto a filter will have a 50% efficiency cut point of 10 μm AD. The design of the size selective inlet giving this cut point must also address the slope of the efficiency curve as the steeper the curve the more sharp the cut point and the fewer oversized particles are collected (QUARG 1996).

With respect to the discussion of particulate matter and its impact on the human respiratory system, three additional fractions have been identified and defined. These are the inhalable, thoracic and respirable fractions. The inhalable fraction refers to the mass fraction of SPM that can be inhaled through the nose or mouth; (generally ≤100 μm AD but often those ≤15.0 μm AD). The thoracic fraction is the mass fraction penetrating beyond the larynx; (generally ≤10 μm AD). The respirable fraction refers to the mass fraction penetrating to the deep lung; (generally ≤4.0 μm AD).

4.2 Methods Of Measurement

4.2.1 Fractions Commonly Monitored

Below is a brief description of the more commonly monitored particulate fractions. The monitoring of such fractions has become commonplace across the globe. A more full discussion of the methods available and design considerations can be found in Appendix C.

One of the leaders in monitoring and legislation is the USA whose government (via the Environmental Protection Agency USEPA), has legislated to control the levels of PM_{10} and $PM_{2.5}$ in urban aerosols. Legislation of this type, World Health Organisation (WHO) directives and the European Union (EU) directives, have led to the standardisation of monitoring techniques and the widening of monitoring networks. This has resulted in the availability of continuous data to show trends and to supply data that can be linked into epidemiological studies. Other fractions are sampled and analysed for various reasons, these are not generally monitored over long enough time periods to offer any idea of prevalent patterns. PM_1 is not commonly monitored but was included in this study to clarify its relationship to other fractions (PM_{10} and $PM_{2.5}$), to investigate the contribution made to these fractions and to assess the viability of monitoring for it.

4.2.2 The Historical Relevance of Various Definitions

The general history of airborne particulate pollution controls is outlined in Table 2. The BS method was introduced in the UK during the 1950's as a simple method for the determination of air quality during the smogs (smoke-induced fogs) of the 1950's & 1960's. It was recognised in the USA that the BS method reflected only one aspect of the ambient aerosol and the TSP methodology was introduced as a way of determining the total atmospheric particulate loading. It was later recognised that health effects attributed to particulate pollution were more attributable to the fraction of SPM/TSP that penetrates beyond the nasal cavity (the thoracic fraction). Consequently, PM_{10} sampling was instigated as a result of research designed to determine the most relevant fraction for monitoring. Later still, information indicated that the respirable fraction was the most toxic fraction, consequently, the USA instigated co-located $PM_{2.5}$ (and PM_{10}) monitoring. Co-located monitoring was recently incorporated into the UK's automatic air quality network to provide data for research.

Table 2: Some legislation with respect to ambient particulate loading.

YEAR	AUTHORITY	FRACTION	METHOD	LIMIT VALUE
1956	UK	BS	STAIN METHOD	(combined with SO_2)
1971	USEPA	TSP	HIGH VOL SAMPLERS	-
1978	USEPA	PM_{10}	SIZE SELECTIVE SAMPLERS	50-150
1980	EC	TSP & TP(BS)	STAIN & HIGH VOL METHODS	TSP 150-300 BS 80-130
1987	WHO	TSP, BS & TP	STAIN, HIGH VOL & SIZE SELECTIVE METHODS	TSP 50-125 BS 120 TP(~PM_{10}) 70
1989	UK DETR	TSP & SO_2	HIGH VOL SAMPLERS	SO_2 50-125 TSP 100-350
1997	UK DETR	PM_{10}	SIZE SELECTIVE SAMPLERS	50 (24 hr running average.)

All limits expressed as μg m^{-3}

USEPA - US environmental Protection Agency **EC - European Community**
DETR - Department of Environment, Transport and the Regions (UK) **WHO - World Health Organisation**

The UK has now replaced the BS method with PM_{10} monitoring. After consultation with EPAQS and QUARG, The National Air Quality Standard (NAQS) for PM_{10} was set at 50 μg m^{-3}; as a 98th percentile 24-hour running average. This was in line with the US legislation and recommendations from other EU countries, as yet $PM_{2.5}$ has not been employed for this purpose.

However, the debate is open as to the significance of $PM_{2.5}$ or PM_1 as a cut point for fine fraction monitoring in the UK. PM_1 represents the fine fraction (nucleation and accumulation modes) and is therefore possibly more relevant with respect to anthropogenic contributions to the global aerosol and to health outcomes than other measures employed.

4.2.3 Methods for Monitoring Particulates

4.2.3.1 BLACK SMOKE METHOD

The Black Smoke (BS) method was developed in the UK and was the first method for estimating the particulate loading of an aerosol. The air is drawn through a white filter on which a stain develops, the darkness of which is dependent on the stain diameter, sample volume and particulate or smoke concentrations. The darkness is measured using a reflectometer. A standard calibration curve or conversion table converts the darkness index to an equivalent particulate concentration. This method

has been used extensively in national networks for the measurement of smoke concentrations, and remains in use to ensure the continuity of historical data collection

The major advantage of this method is its simplicity, no special knowledge is required to understand or operate the equipment and, as the results are obtained using a reflection method, there is no need for expensive equipment and acclimatising facilities. The system allows for eight samples to be collected over 24 hour or 3 hour periods, reducing the man hours required for monitoring. Overall it is a simple and relatively cheap method requiring low maintenance.

The major short fall of this method is the relevance of the results obtained which are easily questioned on the following points. In the first place, this is not an accurate method - variability in measurements can be attributed to the lack of specific, detailed protocol. Specificaly the length and diameter of inlet hose is arbitrary, the flow rate is not monitored, the timers used are not high quality and most significantly the method of analysis has a relatively low resolution. Also, this method relies on the presence of dark carbonaceous matter within the ambient aerosol. This may be relevant in itself, but as a measure of the ambient aerosol, it is not representative, as ratios of such carbon to other components will vary depending on the variations of the many sources. In addition to this, the calibration curves were developed in the sixties and are no longer valid as the overall nature of the urban aerosol has changed since their development, the loss of old sources and the addition of new sources has resulted in a new aerosol composition. Given that the main source of dark carbon in the urban aerosol is vehicle exhaust emissions (QUARG 1995, 1993 (a), 1993(b)), and that elemental carbon absorbs and carries hydrocarbons, BS monitoring results may be relevant to the assessments of health impacts.

Inter-laboratory comparisons during the PEACE study questioned the use of Whatmans No 1 filters (standard for the BS method). The superior efficiency of the membrane filters for sub-micron collection and surface as opposed to internal collection resulted in higher results being recorded (Hoek *et al.* 1997). As the system relied on stain/mass relationships results will have been relevant whilst the conversion tables remained relevant. However, modern aerosols tend to stain less than their predecessors and therefore a redesigned protocol and conversion table may well be required.

4.2.3.2 IMPACTORS

Impactors use the inertia of particles to provide a cut-point at a given aerodynamic diameter. This is achieved by controlling the flow rate and the gap between the inlet and impaction surface. The sample is impacted onto a surface which may or may not be greased to improve the impaction rate (i.e. avoid particle bounce). This device can be used as a sampler in its own right, collecting the fraction impacted, or as a pre-separation device for monitors. In the latter case the impactor is used to remove particulates over a certain size (i.e. PM_{10}) allowing everything below that size to be collected on a filter.

The advantages of the impaction system are that it employs a tried and tested technology which is:

- predictable,
- relatively cheap,
- can be used on small to large scale samplers.
- The virtual impactor has the added advantage that it separates the fine and coarse fractions, which can then be analysed separately.

The disadvantages are:

- a tendency for such sampler heads to be made with poor quality control resulting in a range of results for different heads,
- impaction plates often require cleaning with solvents and re-greasing over relatively short sampling periods (days),
- in some cases these heads can be bulky.

Inter-laboratory comparisons conducted during the PEACE study reported variations of up to 50% between some designs (Hoek G *et al* 1997). This is explained by the differences in greasing procedure (or lack of) and as a result of differing design parameters and tolerances.

4.2.3.3 CASCADE IMPACTORS

Cascade impactors separate the aerosol into different fractions according to their aerodynamic diameter. This is done by forcing the airflow through progressively smaller holes and through progressively smaller gaps, which operate as a sequence of preseparators. In each case the air stream entering the stage contains the fraction below the cut off point of the stage above. Drawing air into

the stage through precisely sized entry holes controls the air stream velocity. Decreasing the size of these holes increases the air stream velocity and therefore the inertia of the particulate matter, whereas the separation between the inlet and the impaction surface controls the flow stream of the air. When the curvature of the flow stream is sharpened, and/or the particle velocity/inertia is increased, the cut point of the stage is decreased.

The heavier particles in each stage are impacted due to their inertia, either onto a filter or suitable collection surface. A back-up filter collects everything passing beyond the final stage, in some cases this may be significant as impaction deposition is not effective bellow around 0.5 μm AD. The loadings of the stages are either determined gravimetricaly or in real-time if using crystal based technology.

The outstanding advantage of a cascade impactor is its ability to provide information on the size distribution of a given aerosol. Prolonged use of such an instrument could give information on the temporal changes in this distribution which may or may not be reflected in the overall measurements being taken. Another advantage is the speed at which results may be obtained; gravimetric based systems require weighing procedures and are no faster than other gravimetric systems, whereas crystal-based systems offer the capacity to collect data sets within 15 minutes (depending on the ambient concentrations). Such systems can be of great use when conducting initial site investigations prior to long term monitoring.

The disadvantages of these systems are:

- that they are precision equipment requiring experienced operators for precise operation,
- the typically short sample periods,
- the time delay if the system is filter based,
- the generally low resolution of the results.

The PEACE study showed a small positive trend in the consecutive weighing of several filter types at the five laboratories (Hoek G *et al* 1997). This was interpreted as being due to handling and was considered as being of little significance to overall PM concentrations. However, this does serve to show how the most stringent of measures must be taken to avoid errors.

4.2.4 Preseparators

As mentioned previously, impactors are frequently used to separate the fraction being sampled from the total aerosol. Another device commonly used for this purpose is the cyclonic preseperator. In this device, the sampled ambient aerosol is drawn into the top of a conical chamber causing the air stream to be forced down the out side of a vortex and, therefore, accelerated. On reaching the bottom of the vortex the air stream is drawn up through the centre of the vortex in a tight spiral flow. By controlling the geometry of the cyclone and the flow rate of the sampled aerosol, it is possible to calculate the size of the fraction caught in the air stream, the size range above is ejected due to its own inertia. Any particulates left in the air stream can then be analysed using the required system i.e. impaction or filter based.

4.2.5 Gravimetric Techniques

In the UK, the most commonly used gravimetric sampler is the Warren Spring M-Type Sampler, using an open face filter, filter holder, gas meter and pump. PM_x is now also widely monitored using both cyclonic and impactor based size selective heads, filter, and filter holder, volume monitoring method and pump. In the case of all these methods, the filters are weighed and re-weighed (after exposure) under climate controlled conditions.

The advantages are;

- the unequivocal mass results obtained,
- the retention of the sample allowing for the analysis of the samples for constituents given suitable filter and loadings,
- methods are easily standardised against reference methods such as the Tapered Element Oscillating Microballance (TEOM) monitors manufactured by Ruprecht and Pattaschnic for PM_{10} monitoring) ,
- the ability to gain information on concentrations of fractions relevant to health.

The most outstanding disadvantages of this methodology are;

- the time and manpower consumed, which leads to delayed results and high costs,
- the methods involved require long monitoring periods to allow for weighable samples to be collected and, therefore, to minimise the errors,
- the data collected is average data for a given sampling period and no real time data is provided.

4.2.6 Tapered Element Oscillating Microbalance (TEOM)

The automatic urban network (AUN), established to provide a network of information concerning particulate concentrations across the UK, uses TEOM monitors. These provide near real time analysis of particulate concentrations at their siting. The system utilises the phenomena that the frequency of a crystal will change proportionally with a change in its mass. Air is drawn through a size selective head onto the filter cartridge which sits on a tapered element in the sampler, as the mass of particulates increases the element oscillates more slowly, this change in frequency over time is converted to a mass concentration. To avoid problems associated with humidity, the system heats the inlet behind the inlet head to 50°C, driving off excess water and some volatile organic compounds (VOC's) (QUARG 1993 and 1996).

This system has the advantages of

- low manpower requirements as the filter needs to be changed less often than with a manual system,
- the hourly, daily, monthly and yearly averages recorded,
- the automatic transfer of the data,
- the system also records meteorological data.

This means that the user can get high resolution, near real-time data with reference to local weather conditions without having to dedicate a team of technicians to the job.

The main drawbacks of this system are

- the initial expense (£ thousands per unit),
- the tendency to give 'false' results depending on ambient humidity and the build up of material on the filter.

There is debate as to the significance of the differing results obtained using co-located TEOM systems and other traditional gravimetric methods such as the Partisol 2000 (also made by Ruprecht and Pattaschnic) which tend to give higher results. The reason for the lower readings obtained by TEOMs is the heated inlet which volatilises mass. The intention is to dry the sampled aerosol after passing it through a size selective inlet to avoid over estimation caused by adsorbed and absorbed water and to compensate for the conditioning process used in traditional gravimetric techniques. However, there is concern that the more volatile compounds are also being driven off resulting in

underestimation of particulate concentrations. As a result there is debate concerning the reference methods used for PM_{10} compliance monitoring in the UK, these being set using TEOM data, traditional methods have recorded levels up to 30% higher (*Pers. comm.* ETI LTD 1998).

4.3 Other Common Samplers

Other sampler types are often used and reported, some of these will be described in basic terms before discussing variations in results. The more common types are dichotomous samplers, HiVol samplers, and Beta gauges. This is a n EU standard method and is used extensively throughout mainland Europe (see Table 3)

The dichotomous sampler has the advantage that, using a virtual impaction system, it is possible to separate the sample $\approx$ 10μm AD and the $\approx$ 10 μm AD contained in a PM_{10} sample. This type of monitor is widely available and is a robust machine.

HiVol samplers are designed to collect large samples on large filters, this gives the advantage of reducing error especially if chemical analysis is applied to the filter. They are available as TSP or PM_{10} monitors. Again these systems are widely available and tend to be robust.

Beta (β) gauges collect short-term samples (say 15 mins) on a tape filter. Each of these samples are passed between a beta source and counter. The degree of attenuation caused by the sample is directly related to the mass of the sample. This system has the advantage that it can give near real-time results every 15 minutes. The disadvantage of the varying beta attenuation properties of different aerosols requires on-site calibration of the equipment.

Optical analysers can utilise the light-scattering properties of particulates to measure concentrations. The response of such instruments is very much dependent on the size distribution of the aerosol, shape and refractive index of the particles. As a result, they tend to be more effective in industrial scenarios where the aerosol is well defined and relatively stable in terms of composition. These types of systems can be fitted with size selective inlets, before the sample is fed to a light scattering chamber to be analysed. They can and are used as ambient monitors, with one of their advantages being the speed of results (real time).

Table 3: Measurement devices used in different networks. (SOURCE: World Health Organization)

Country	PM10	TSP
Austria		beta gauge TEOM
Belgium	beta gauge	beta gauge
Germany		beta gauge Small filter device
Denmark filter		sampler
Czech Republic	beta gauge	
Finland	HV sampler	HVsampler
France	beta gauge TEOM	
Hungary	beta gauge	
Latvia		Gravimetry
Lithuania		Gravimetry
Luxembourg	TEOM	
Netherlands	beta gauge	
Poland	gravimetry TEOM	beta gauge
Portugal	beta gauge	HV sampler beta gauge
Romania		Gravimetry
Spain	beta gauge TEOM gravimetry	
Sweden	TEOM	
Switzerland	Gravimetry beta gauge TEOM	
United Kingdom	TEOM	

4.4 Variations in Sampler Efficiencies

During a field comparison of PM_{10} samplers in Europe for the PEACE study (Hoek *et al* 1997), variations in mass concentrations of around 13 to 20% were obtained using co-located PM_{10} Harvard Impactors (the reference method) and local samplers (Table 4). A study in 1995 showed differences ranging from 4.5 to 14% between PM_{10} cyclonic and impactor heads.

Table 4: PM_{10} field comparisons between local monitors ($PM_{10(LOCAL)}$) and Harvard reference monitors ($PM_{10(HA)}$) in the PEACE study. Co-locatedsamplers, winter 1993/94. Hoek G *et al* (1997)

CENTRE	LOCAL SAMPLER	a+b*	SD§	R^2	MEAN DIFFERENCE ($\mu g\ m^{-3}$)	DIFFERENCE (%)	NO OF SAMPLES
Amsterdam	Dichotomous	-1.4+0.93	5.2	0.93	-4.6	-12.5	45
Teplice	Hivol	-1.3+1.19	3.3	0.87	+2.2	+4.7	15
Pisa	Hivol	-19.3+1.30	3.6	0.65	-3.8	-8.2	10
Oslo	Dichotomous	-0.9+1.23	0.7	0.98	+3.4	+16.4	15
Oslo	Dichotomous	-2.0+1.30	0.7	0.93	+3.1	+16.3	14
Budapest	β gauge	6.0+1.06	1.4	0.99	+7.6	+17.7	9
Budapest	β gauge	2.4+1.23	1.3	0.91	+7.4	+19.6	8

*Where: $PM_{10(HA)} = \underline{a}+(\underline{b}\times PM_{10(LOCAL)})$ § SD = Standard Deviation

It can be seen from Table 4 that the Hivol in Pisa was oversampling in comparison to the Harvard Impactor and that this had the lowest correlation of the sites (R^2=0.65) suggesting this is the least reliable sampler.

The remaining samplers showed a strong correlation with the Harvard Impactor, this suggested that the same fraction is being sampled but with a systematic "error" or difference (as the true value is unknown). This was especially the case with one of Budapest's β gauges (R^2=0.99) and one of the Oslo dichotomous samplers (R^2=0.98). This loss or difference was partially explained by Hoek *et al* (1997), as being due to a combination of inlet design and greasing of impaction plates.

The β gauges in Budapest showed systematic undersampling, given this and the high degree of correlation with the Harvard impactor, it is reasonable to presume that this is a consistent systematic error, which could be accounted for by using a suitable calibration factor. All other samplers show a negative intercept, which indicates oversampling at low concentrations. In contrast, the difference between the actual samples ($PM_{10(Ha)}$ and $PM_{10(local)}$) indicates undersampling at high concentrations.

This apparent contradiction is possibly a reflection of changes in sampling efficiency under different conditions i.e. wind speed etc. It is possible that the 'true' correlation is more complex than a straight-line model and it is reasonable to assume that it would pass through the origin given sufficient resolution.

4.5 Effects of Humidity

Humidity and temperature effect the weight of filters and samples, depending on the hygroscopic properties of both. As the particulate levels being monitored are minute this often effects the results. All filters and samples are therefore, conditioned at a standard humidity and temperature prior to weighing.

With respect to ambient aerosols, ionic material, such as NaCl, will increase in mass and size with increases in relative humidity (RH) as they are hygroscopic. Hitzenberger *et al* (1995) took impaction foils from previously sampled aerosols, re-weighed them at various RH's, and demonstrated that the bulk of such material was found in the accumulation mode. This was the fraction that had shown the greatest mass increase factor (wet mass/dry mass) and, therefore, this is the aerosol fraction most affected by variation in ambient RH. Mass increase factors of 3.9 were found at 95% RH for the 0.5-1.0 μm AD fraction whereas the 8.0-16.0 μm fraction showed a mass increase factor of 1.4 at 95% RH. These findings were characteristic of the specific aerosol used in the study, the abrupt changes being related to the thermodynamic properties of the chemical fraction responding.

Busch *et al* (1995) demonstrated that the diameter of a monodisperse NaCl or KCl aerosol changes diameter at a given RH, which is specific to the chemical in question. The different growth curves being the result of the thermodynamic properties of the salt in question, NaCl showed a growth factor of 1.75 at around 73% RH whereas KCl has a growth factor of 1.8 at around 84% RH. This abrupt change in diameter at a given RH, an individual salt's growth point, will effect the changes in overall size distribution of ambient aerosols with changing levels of RH. Specific chemical fractions changing size and mass at their own growth points. This will mean that there will be an RH value below which there is a negligible impact, this corresponding to the lowest RH at which any component of the aerosol will be affected. Busch *et al* (1995) also showed that the sub-micron fraction of an ambient aerosol displayed distinct hydrophobic and hydrophilic fractions, reflecting the complex composition of airborne particulate matter.

4.6 Results of Urban Aerosol Studies

Table 5 below shows the results from several recent studies of particulate levels in various parts of the world. It can be seen that $PM_{2.5}$ monitoring has recently been introduced and all the results shown here are taken from the Enhanced Urban Network in the UK. The numbers seem low in some cases but as the sites had only been operational for a few months when this data was down loaded they are not representative of yearly averages. The same sites show that $PM_{2.5}$ typically accounts for between 50 - 80% of PM_{10} depending on weather conditions and season.

The PEACE study showed the range of values for PM_{10} recorded at sites across Europe. This demonstrated the variations in levels, however, the results showed a definite spatial distribution of concentrations with the highest concentrations in the south (see section 4.7). Other studies in the UK have shown PM_{10} concentrations ranging from 15 to 160$\mu g\ m^{-3}$, these levels are typical for urban sites in western countries.

Table 5 : Ranges of results from some recent studies of urban aerosols, and from DETR AUN air quality information site on the Internet.

FRACTION	METHOD	AVE $\mu g\ m^{-3}$	PERIOD	SOURCE
$PM_{2.5}$	TEOM	18-72	24 hr	AUN (1998)
$PM_{2.5}$	TEOM	16-21	24 hr	Harrison R M et al (1997)
PM_{10}	TEOM	16.5-24.7	24 hr*	Harrison R M et al (1997)
PM_{10}	Partisol	15-120	24 hr	Smith S. et al (1995)
	TEOM	10-110		
PM_{10}	TEOM	15-85	24 hr	AUN (1998)
PM_{10}	TEOM	15-40	Monthly	Smith s. & Jinpeng (1994)
PM_{10}	TEOM	15-50	Monthly	QUARG (1996)
PM_{10} (indoor)	Impactors	23-50	24 hr	Liou et al (1988)
PM_{10}	Beta gauge	50-190	24 hr	Tsai C-J & Cheng (1996)
PM_{10}	Various	1-205	24 hr	PEACE study: Hoek et al (1997)
TSP	Hi Vol	20-160		
BS	Stain method	<10-60	24 hr	Reponen et al (1996)
PM_{10}	M&T impactor	<10-160		
BS	Stain method	7-103	24 hr	Williams I et al (1995)
TSP	high vol	14-135	24 hr	
		11-1091	Rush hr	
BS	Stain method	1-238	24 hr	PEACE study: Hoek et al (1997)

* **Averaged: winter-summer.**

4.7 Relationships Between PM_{10} and BS (from the PEACE study)

The European PEACE study (Hoek *et* al 1997) showed a wide range of PM_{10}/BS ratios ranging from 0.67 to 3.67, with several cases of BS being in excess of the corresponding PM_{10} value. Six urban centres showed lower concentrations than surrounding rural areas, this was explained by the individual, decentralised coal and wood fired heating typical in rural central Europe as opposed to district heating which is commonplace in urban areas. Long-range transport of aerosols were inferred from the strong urban-rural BS correlations (Table 6), which are slightly better than equivalent urban-rural PM_{10} correlations. Hoek concluded that his and other studies showed PM_{10} and BS correlations to be highly dependent on time, site and season. Such data is, therefore, difficult to transform from PM_{10} to BS or vica-verca. This is not surprising given the nature of BS monitoring and the age of the calibration charts used. In conclusion BS is an ambiguous reference to levels of particulate pollution, requiring up to date and possibly site-specific calibration curves. The BS method is best only applied to provide comparison data and this assumes no changes in aerosol composition.

Table 6 Spearman correlation coefficients for urban and rural PM_{10} , urban and rural BS, urban PM_{10} and BS and rural PM_{10} and BS (from the European PEACE study: Hoek G *et al* 1997).

City	Urban-rural correlation		PM_{10}-BS correlation	
	PM_{10}	BS	Urban	Rural
Umea	0.74	0.71	0.71	0.75
Malmö	0.71	0.76	0.57	0.44
Oslo	0.78	0.80	0.81	0.80
Kuopio	0.87	0.86	0.81	0.85
Amsterdam	0.91	0.93	0.81	0.80
Berlin	0.90	0.91	0.73	0.78
Hettstedt	0.77	0.65	0.60	0.67
Budapest	0.76	0.60	0.57	0.81
Katowice	0.86	0.81	0.89	0.93
Cracow	0.77	0.66	0.75	0.84
Prague	0.80	0.82	0.95	0.76
Teplice	0.46	0.49	0.92	0.75
Pisa	0.87	0.85	0.80	0.85
Athens	0.74	0.83	0.89	0.87

4.8 Relationships Between PM_{10} and $PM_{2.5}$

Table 7 shows a range of correlations found between PM_{10}, $PM_{2.5}$ and a range of other pollutants in a Birmingham study (Harrison 1997). It can be seen that there is a strong correlation between the two

fractions R^2=0.86. Similarly, Brook (1997) found strong correlations with R^2 values ranging from 0.82 to 0.94 in a study of PM_{10} and $PM_{2.5}$ at nine sites across Canada. The same study showed long-range transport of both fractions across the country, resulting in a high degree of spatial correlation in day to day variations and inter-site correlations.

Table 7: Correlations for PM_{10} and $PM_{2.5}$ V's several pollutants, temp and wind speed at Hodge Hill, Birmingham between March and June 1995 (Harrison R M *et al* 1997)

POLLUTANT	PM_{10}	$PM_{2.5}$
COARSE	0.72	0.27
PM_{10}	1.00	0.86
$PM_{2.5}$	0.86	1.00
OTHER	0.80	0.51
CL^-	0.15	0.10
EC	0.68	0.75
NH_4	0.50	0.61
NO	0.54	0.70
$N0_2$	0.71	0.76
NO_3^-	0.52	0.67
NO_X	0.60	0.74
SO_2	0.63	0.57
SO_4	0.66	0.68
TEMP	0.23	0.14
WIND SPEED	-0.32	-0.50

However, as PM_{10} contains a coarse mode component not present in $PM_{2.5}$ (i.e. the resuspended dust element), the observed correlations will reflect long term patterns whilst obscuring the short-term changes due to coarse mode excursions. For example, Harrison *et al* 1997 showed that on 25/08/95, a sharp peak in PM_{10} did not correlate with $PM_{2.5}$ but was correlated with a peak in wind speed. It was concluded that this effect was due to the resuspension of street sediments and soil. It is events like this that weaken the observed relationship between the two fractions, particularly when obsevations are made on a short-term basis. In contrast to this, on bonfire night 1994; combustion-related events resulted in identical patterns of PM_{10} and $PM_{2.5}$ elevation, with the latter accounting for >90% PM_{10}. This is the general pattern for winter data, with the resuspended particulate element being much reduced in cold and wet conditions.

During the Birmingham study, $PM_{2.5}$ was seen to correlate more strongly with EC and most ionic species than did PM_{10}. However, both $PM_{2.5}$ and PM_{10} were similarly correlated with NO_X, SO_2 and SO_4 whilst Cl^- was poorly correlated with both fractions. The stronger correlations indicated traffic as a source of particulates during this study at this site.

5. SITE DESCRIPTION

The monitoring site for this project was situated on the Archway Road (A1) on the outside balcony of The Winchester Hall Tavern (post code : N6 5BA map ref. TQ289877) . The A1 is a two lane red route at this stage and becomes dual carriageway two hundred meters down hill to the South-east (see Figure 8). Further North-west the A1 joins the M1 at junction 2. In the section between Archway underground station and Highgate underground station the A1 is a busy urban highway carrying buses, taxis, goods vehicles, local traffic and commuters (see Figure 8).

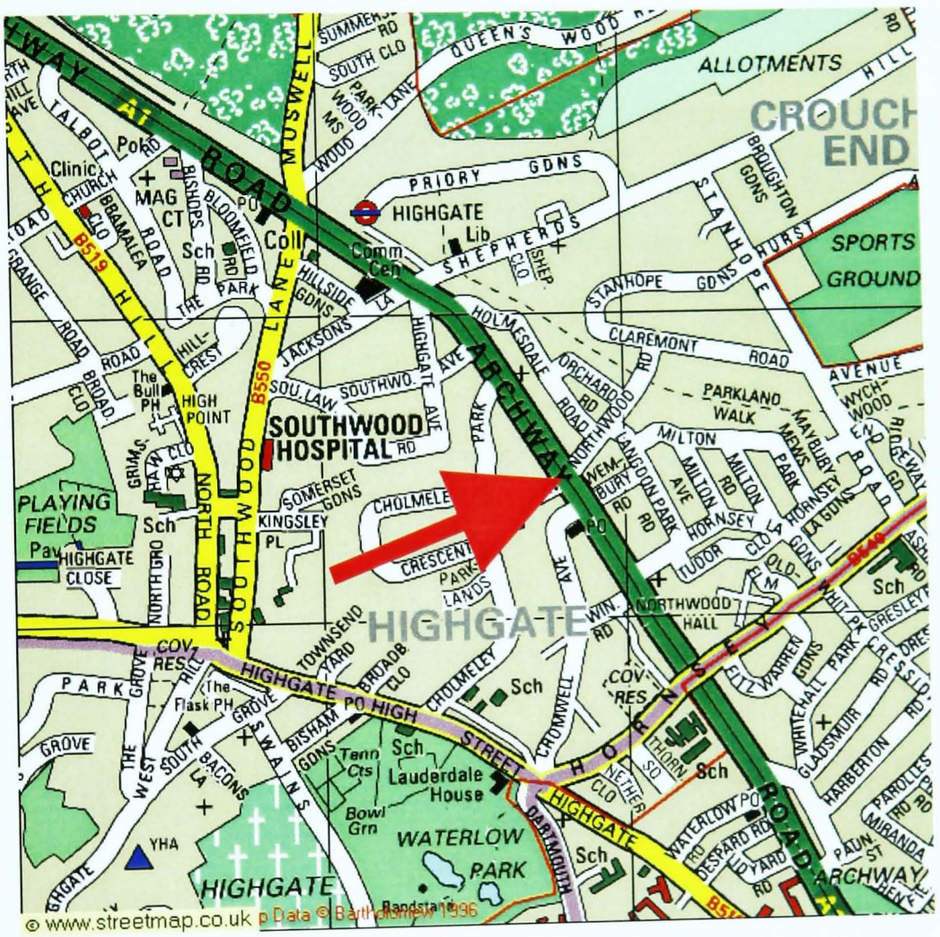


Figure 8: Site map for sampling site on Archway Road.

The sampling site was located at a height of 5.1-5.8 m above the street, which in itself was at an elevation of ≈100 m, on a hill roughly 70 m above the mean level of London (OS grid reference 290877 Landranger sheet 176). The Partisol system was placed on the balcony above and behind the AirMetrics, TSP inlets and BS inlet, which were hung over the balcony 70 cm lower and 1 m further into the road. The entire sampling area covered an area 1m × 1.8 m (see **Error! Reference source not found.**). The entire site was set up in as small an area as possible to maintain the integrity of the samples as being co-located.

The site itself was chosen to represent the Highgate/Crouch End section of the A1 as this was the area most relevant to SWAG. Given the limitations of site placement (i.e. security, access, power, representation of chosen pollutant etc) the final choice for the site was believed by the author to give all aspects equal consideration. The possibility of particulate interference from within the building was considered to be minimal and acceptable given the options. The urban canyon effect known to exist in this area was considered to be outside the scope of this study. Attempts were made to gain traffic flow figures from Harringey Council but the author was advised that there were no figures relevant to the site. Such data would have been crucial in any attempt to define the contribution of traffic to particulate concentrations.

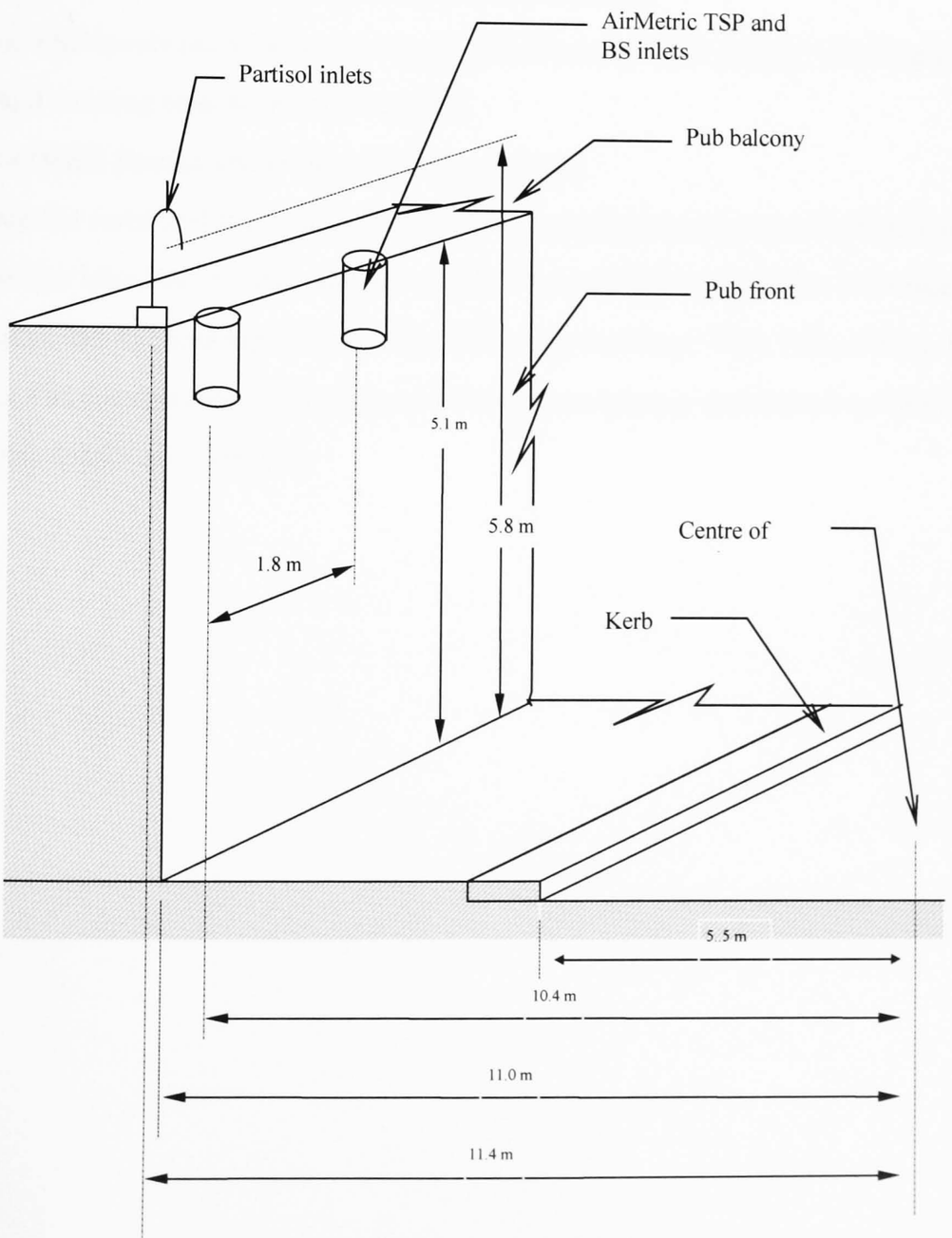


Figure 9: Schematic for layout of the sampling site at Archway Road

6. Aims and Objectives

The aim of the project was to characterise ambient particulate air pollution at Archway Road, a roadside site in greater London. Characterisation was to be achieved through establishing correlations between various fractions of ambient suspended particulate air pollution for the duration of this study. These fractions were collected using various instruments and methods. The specific objectives of this study were to:

- Monitor PM_{10} levels (as a 24-hour average) using an AirMetric™ MiniVol sampler.
- Monitor PM_{10}, $PM_{2.5}$ and PM_1 levels (as 24 hour averages) using the Rupprecht and Pattaschnic Partisol 2000 Starnet system (USEPA reference method).
- Monitor TSP levels (as a 24 hour average, and concentrations during: morning rush hour 06:00-10:00 and evening rush hour 16:00-20:00).
- Monitor Black Smoke levels (as a 24-hour average).
- Compare the results of the two co-located PM_{10} monitors and assess the degree of correlation between the MiniVol™ PM_{10} monitor and the Partisol 2000 (a USEPA reference method).
- Investigate the relationships between the following fractions; TSP, PM_{10} $PM_{2.5}$, PM_1 and BS.
- Monitor PM_{10} levels during morning and evening rush hours (combined samples) using an AirMetric MiniVol™ sampler.

7. METHODOLOGY

7.1 Equipment and Operating Conditions

7.1.1 Monitoring of TSP

All the systems described bellow were arranged on site as to give simultaneous, collocated samples. This meant that the monitors were placed as close to each other as possible without interfering with each other or the ambient nature of the sample.

Three Rotheroe and Mitchell pumps were used for the monitoring of TSP. One L30, drawing approximately 30 L min^{-1} for 24 hour samples and two L100's drawing approximately 100 L min^{-1} for rush hour samples. These units consist of a high quality pump, an integral flow meter and an open face filter housing. The filter housing supplied was extended using suitable fittings and hose to be situated remotely, allowing for the pumps to remain dry and for filter housings to be mounted face to the street with rain shielding cowls. 24 hour timers were employed to obtain the sample periods required, these were set to obtain one 24 hour sample (12:00 to 12:00), one morning rush hour sample (06:00 to 10:00) and one evening rush hour sample (16:00 to 20:00) per day.

In the pilot study (appendix B) the L30 was found to draw between 32 to 34 L min^{-1} and the two L100's were found to draw between 88 to 93 L min^{-1} and 79 to 85 L min^{-1}, respectively. Variations were partly due to the loading on the filters but flow rates were found to be stable to within 3 L min^{-1} during any one sample run by recording flow rates before and after sample runs.

Volumes of air sampled were determined using three dry gas meters in series with the pump and filters. Therefore actual flow rates are not crucial, it was only necessary to ensure a suitable sample volume for accurate analysis. Meter readings, flow rates and filter numbers were logged for each sample station each day.

7.2 Monitoring of PM_{10} with AirMetric Minivol™ Monitors

Two AirMetric MiniVol™ portable monitors (see Figure 10) were used to monitor PM_{10}. These monitors utilised an impaction pre-separator to achieve a 10 μm AD cut point. The filter housing was incorporated into this unit which was fitted to the monitor via a snap-lock fitting see Figure 11

Figure 10: The AirMetric monitor (provided by SWAG)

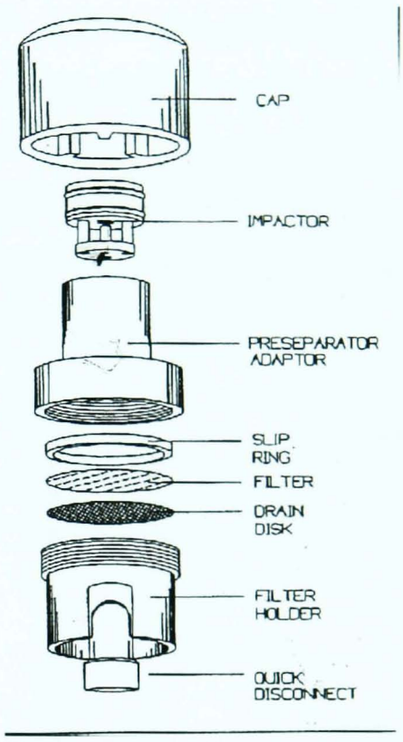


Figure 11: Schematic of PM_{10} inlet

These monitors operated at a flow rate of 5 L min^{-1} which was guaranteed by an internal flow meter and an integral flow control circuit. Low flow rates result in shut down of the monitor; this was verified as being accurate in the pilot study. The monitors were battery powered using large purpose built, rechargeable powerpacks, allowing for sample runs of up to 24 hours. Powerpacks were recharged on site in waterproof boxes, using the transformers supplied. Internal circuits shut down the monitor if the battery was at low power to safeguard the life of the battery.

Internal timers allowed for a range of sample periods to be pre-programmed and an internal time elapsed clock recorded sample time in 100th's of an hour. Sample times, battery numbers, filter numbers and flow rates were recorded before and after each sample run. Samples were taken for 24 hour (12:00 to 12:00) and rush hours (06:00 to 10:00 and 16:00 to 20:00 on the same filter) periods.

PAGE

NUMBERING

AS ORIGINAL

7.2.1 Monitoring with the Partisol 2000 Starnet System

A Partisol 2000 Starnet System was used to monitor PM_{10}, $PM_{2.5}$ and PM_1. This is a USEPA PM_{10} standard method, consisting of one hub unit and three satellites. The hub contained a mains powered pump, switching gear and control circuitry. The satellites (and hub) contained a filter housing and pre-separator connected to the hub via 3m of airline. User-defined programming of the unit gave up to eight sample periods, two per station and full control of flow rates. Information was logged: sample station in use, ambient temperature, pressure, system status, sample dates, time, total volume and standard volume sampled (relative to 20^0C and 1 atmosphere), sampling time and valid sampling time (on a half hourly basis and a sample run basis). This information was stored in a circular buffer, allowing for up to 2 months data to be stored. This was retrieved as a comma separated data stream, using the relevant software via an RS232 link (this can be remote).

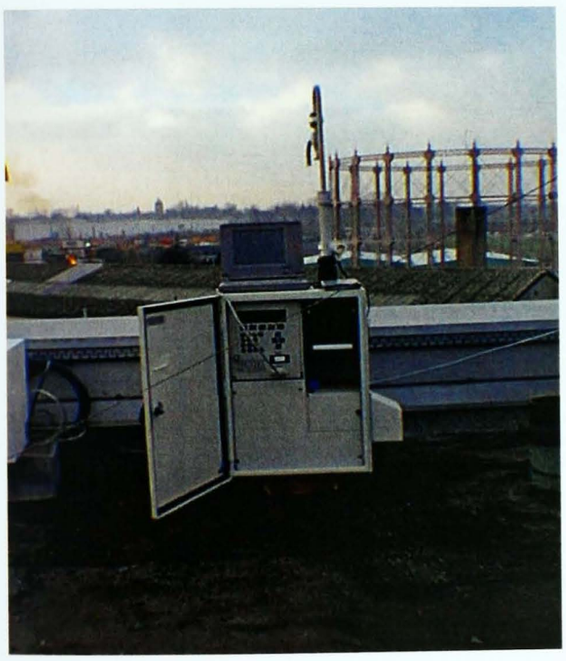


Figure 12: The Partisol 2000 'Hub' fitted with cyclonic $PM_{2.5}$ inlet and laptop down loading stored data

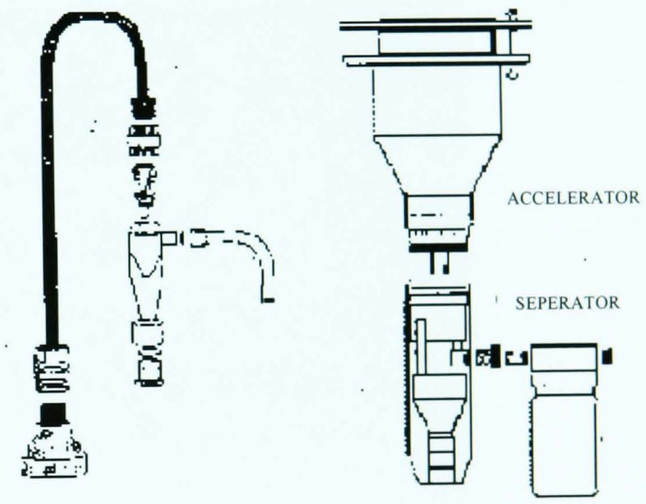


Figure 13: Schematics for cyclonic $PM_{2.5/1}$ heads and impaction based PM_{10} head

The PM_{10} pre-separator used was an impaction system. $PM_{2.5}$ and PM_1 pre-separators were both cyclonic the cut points of all the pre-separators were achieved at 17.6 L min^{-1} (approximately 1 m^3 sample volume $hour^{-1}$). Control circuitry monitored the flow rate and maintained it at ± 5% of this value or considered the volume sampled outside this limit as invalid. The system was programmed to sample for 24-hour periods (12:00 to 12:00) sequencing through all stations on a five minute basis (Hub, Sat1, Sat2, Sat3, Hub, Sat1, Sat2 etc.).

7.2.2 Monitoring Black Smoke

Black Smoke (BS) was monitored using an 8 port sampler. The sampler allowed for continuous monitoring and could switch from port to port on a 3 or 24-hour basis using an internal timer. The port currently monitoring was indicated by running the exhaust air through distilled water (bubbling indicating the port in use). The sampler was set to monitor 24-hour samples, filters being changed every 7 days and taken to the lab for analysis.

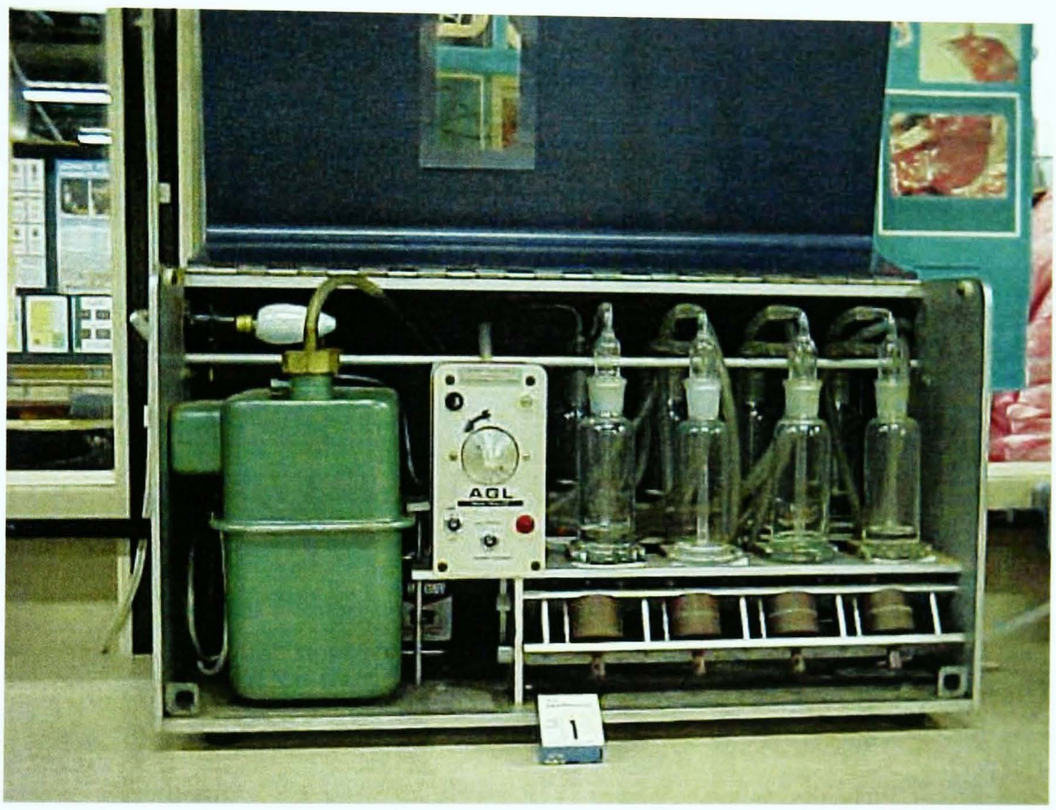


Figure 14: The black smoke sampler with side open showing gas meter, timer, bubble jars, filter clamps and a box of filters.

The inlet for BS was situated on the frame, over the balcony wall and in close proximity to the TSP heads and MiniVol samplers. The inlet consisted of an inverted funnel connected to the sampler by approximately 1m of 1cm diameter tube. The tube was arranged in such a fashion as to ensure the most direct path to the sampler. The sampler operated at a flow rate of around 64 ft^3 day^{-1} and the internal gas meter gave the sampled volume. Readings from the gas meter were recorded at switching time (12:00 hours) every day.

7.3 Filters and their Treatment

7.3.1 TSP Monitoring

For the monitoring of TSP; Whatmans GF/A 60mm diameter glass fibre filters were used. These were placed in labelled 90mm diameter, clean, single vent, plastic Petri dishes and conditioned for 24 hours in clean box facilities under dust and humidity controlled conditions. The filters were weighed under these conditions on a five figure Ohaus microbalance; humidity, temp, filter ID's and weights were recorded. The balance was calibrated before and after each weighing period (4 hours) (this was found to remain stable during the pilot study). Filters were re-weighed after a further 24 hours conditioning and weights were compared, differences over ±10 μg were considered unacceptable and any such filters were reconditioned and weighed until consecutive weights met the requirements. Any filters which are outside of the tolerances after five weighings were not used. The average of the two consecutive weighings were taken as the clean filter weight.

Filters were never be handled - Whatmans filter tongs were always be used to manipulate filters. Filters were placed into their labelled Petri dish and into two re-sealable plastic bags for transportation.

Filters were stored on site in two re-sealable plastic bags and only taken out during sampling. For sampling the filters were placed into the snap-on housing and exposed as per the sample regime. Filters were changed at 12:00 daily and records kept of which filter was exposed when, filters were immediately replaced in their Petri dish and two re-sealable bags for storage and transportation back to the laboratory for analysis.

Filters were conditioned in their Petri dishes in the clean box facilities for a minimum of 24 hours before weighing as above on the same five figure balance. Again the average of the two consecutive weighings which met the criteria (±10 μg) was taken as the exposed mass.

7.3.2 PM_x Monitoring using Partisol and AirMetric Monitors

For the monitoring of all PM_x fractions; Palflex 47mm diameter, Teflon-coated glass fibre filters with integral PNP support were used. Filters were placed in 50 mm labelled, clean, single vent Petri-

dishes in the clean room facilities under temperature, humidity and particulate controlled conditions for a minimum of 24 hours conditioning. Filters were weighed on a Cahn 32, six-figure microbalance. Filter number, temperature, humidity and mass were recorded. Repeat weighings were made after 24 hour conditioning periods and, given a precision of ±10 μg, the average of the two weighings was taken as the clean mass. Any filters outside the required tolerance were re-weighed until consecutive weighings were made inside the tolerance. Any filters failing to give consecutively precise weighings were not be used. The microbalance was calibrated before weighing and after every ten weighings, if a tolerance of ±3.0 μg was exceeded for the zero or calibration weight (200 μg) all ten previous weights were disregarded and filters were re-weighed. If the conditions in the clean room changed by ±10% RH or ± 5^0C weighing was not attempted, or if in progress was stopped and filters weighed during that period re-weighed later.

Figure 15: The author using the Cahn micro-balance in the Middlesex University clean room faccilities.

Any filters showing evidence of static charging were neutralised by passing through ionised air, generated using two alpha sources. Filters for the Partisol were loaded into their labelled filter cases and two re-sealable plastic bags in the clean room. Filters for the AirMetric MiniVols were loaded into their labelled filter housing, which was integral to the pre-separator heads, and two re-sealable plastic bags in the clean room for transportation and on-site storage. Partisol filter holders were loaded into the filter housing for exposure and exposed filters sealed in two re-sealable plastic bags. AirMetric MiniVol heads were fitted to the sampler and heads containing the exposed filters were sealed in two re-sealable plastic bags for later analysis.

Filters were replaced into the relevant labelled Petri dishes in the clean room facilities, conditioned for a minimum of 24 hours and weighed according to the procedure described above. The average of the two consecutive weighings meeting the tolerance requirements was taken as the loaded mass and recorded.

7.3.3 Black Smoke (BS) Monitoring

For the monitoring of BS; 25 mm diameter Whatman Number 1, paper filters were used. The black smoke method requires no pre-treatment of filters. The filters were transported in their box, in two resealable plastic bags. The filters were loaded into the 8 port sampler by hand and exposed. On changing, the exposed filters were placed in labelled, clean, single vent, 50 mm diameter Petri dishes which were placed into two resealable plastic bags for on-site storage and transportation to the lab for analysis.

7.4 Calculation of Deposited Mass

The samples were conditioned in the clean room for 24 hours and weighed; once before sampling, giving the clean filter mass, and again after sampling giving the loaded filter mass, as outlined above.

The mass of particulate matter collected (M_{PM}) was determined by taking the clean filter mass (FM_C) from the loaded filter mass (FM_L) (equation 1):

$$M_{PM} = FM_L - FM_C \qquad \text{....Equation 1.}$$

This mass was converted to mass per unit volume by dividing M_{PM} by the volume of air that had passed through the filter whilst sampling (V_{STD}) (equation 2):

$$Mass/Vol = \frac{M_{PM}}{V_{STD}} \qquad \text{....Equation 2.}$$

All weights were reported as μg and volume was reported as m^3, hence the final mass concentrations were reported as μg m^{-3}.

7.4.1 Analysis of BS Concentrations

Concentrations of BS were determined using an EEL reflectometer. Consisting of a head fitted with a light source, a light sensitive resistor and an ammeter that registers the current passing through the light sensitive resistor (induced by the reflected light).

The filter was placed on a white tile and a clean portion of the filter was exposed through a hole in a black screen. The reflectometer head was placed over the screen and the meter was set to register 100% reflectance. The screen was moved to reveal an exposed portion of the filter and a new reading was recorded, this was double-checked by reading another area of the exposed filter. The acquired percentage reflectance was recorded as the R-value.

The R value was cross referenced on a calibration table for the stain size (0.5 inch) against the sampled volume (in cubic feet) an equivalent mass per unit volume (in μg m^{-3}) was retrieved and recorded.

8. RESULTS

8.1 Partisol PM_X Data

The data obtained using the Partisol 2000 were collected from 29/06/98 to 08/09/98 as 24-hour averages. Data capture for PM_{10} was 73%, for the two $PM_{2.5}$ satellites was 79% and 74%, and for PM_1 79% data capture was achieved. Losses were due to the loss of filters over the weekend of 04-05/07/98. In addition, a failed attempt to modify the sampling regime resulted in losses over the week 20-26/07/98.

The summary statistics can be seen in Table 8, from this and the time series (Figure 16) it is clear that particulate concentrations decreased in the order PM_{10}>$PM_{2.5}$>PM_1. This would be expected, as the finer fractions are a component of the larger. The ratio of PM_{10}:$PM_{2.5}$:PM_1 was found to be 100:76:62 from their respective mean values (21, 16 and 13 $\mu g\ m^{-3}$, Further analysis of these and other relationships by regression analysis can be found in the discussion.) These results also indicate that levels were between 68 and 38% lower than the NAQS limit of 50$\mu g\ m^{-3}$ (as the 98th percentile of a running 24-hour average) throughout the monitoring period. On average levels were found to be 42% of the NAQS limit. The percentage contribution of $PM_{2.5}$ to PM_{10} was found to be 76%. During this study $PM_{2.5}$ ranged from 100% (31/07/98) to 60% (30/07/98) of PM_{10}.

In those cases where the order of magnitude for the fractions varied from PM_{10}>$PM_{2.5}$>PM_1 (i.e. 06/05/1998 see Figure 16) it is clear that an error has occurred. This is likely to be due to contamination of the sample of the finer fraction or losses from the coarser.

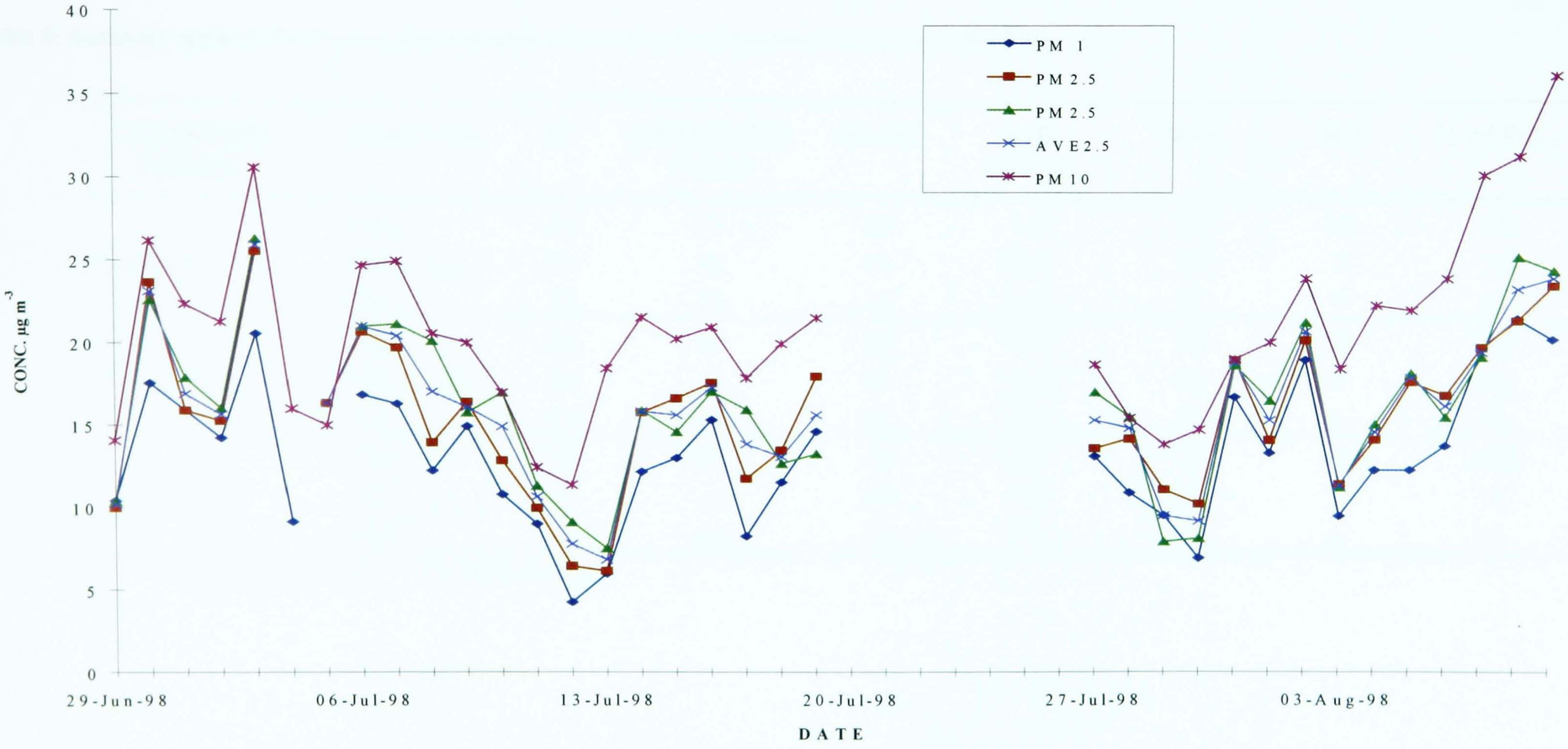


Figure 16: Time series for all Partisol data collected at Archway Road between 29/06/98 and 08/08/98.

Table 8: Summary statistics for Partisol data collected at Archway Road between 29/06/98 and 08/08/98.

AVERAGING PERIOD	FRACTION	N*	ARITHMETIC MEAN	MODE	STD ERROR	MAX	MIN	% of PM_{10}
ALL DATA	PM_{10}	34	21	20	1.0	36	16	100
	$PM_{2.5\ (AVE)}$	33	16	15	0.9	26	7	76
	PM_1	33	13	13	0.7	21	4	62
WEEK DAYS	PM_{10}	25	21	20	0.8	31	14	100
	$PM_{2.5\ (AVE)}$	24	16	15	0.8	26	9	76
	PM_1	25	13	13	0.8	21	6	62
WEEK ENDS	PM_{10}	10	21	19	2.5	36	11	100
	$PM_{2.5\ (AVE)}$	9	15	14	2.0	24	7	71
	PM_1	9	14	12	1.7	21	4	67

* Number of samples. All values in $\mu g\ m^{-3}$

8.2 AirMetric PM_{10} Data

The AirMetric PM_{10} data was collected as 24 hour averages for the period 29/06/98 to 09/08/98 and as combined rush hour (peak traffic) averages for the period 21/07/98 to 09/08/98. Three rush hour samples were lost due to a timer fault (07 to 09/08/98). Data capture of 95% was achieved for rush hour samples and 100% for 24-hour samples.

It is indicated from the time series (Figure 17) and summary statistics (Table 9) that the 24 hour AirMetric PM_{10} levels are consistently lower than the NAQS limit of 50μg m^{-3} (a rolling 24 hour average as opposed to the fixed 24 hour average used in this study). This is true for all but one occasion (30/06/98) where the recorded level was found to be 51 μg m^{-3} (Partisol value 26 μg m^{-3}). This value may be an error as the corresponding Partisol data value is much lower and the rest of the two data sets are in close agreement. Alternatively, this may be due to a high mass-low density particle being captured on the AirMetric filter (i.e. a biological particle with a low AD). This was deemed important when regression analysis was applied in order to compare the two PM_{10} monitors, and the data for that day was excluded from the analysis.

8.3 TSP Data

TSP was collected as 24-hour averages (TSP 24), morning rush hour (TSP RH_{AM} : 06:00 to 10:00) and evening rush hour (TSP RH_{PM} : 16:00 to 20:00). For TSP RH_{AM}, 90% data capture was achieved, 98% data capture was achieved for TSP RH_{PM} and 83% data capture was achieved for TSP 24 (see Figure 18). Data from nine filters were lost due to contamination from their filter holders; 29/06/98 TSP RH_{PM}, 29 to 30/06/98 TSP 24 and TSP RH_{AM}. Data was also lost due to the loss of three filters during bad weather; 02/07/98, 01/08/98, 07/08/98 and 09/08/98 for TSP 24 and 06/08/98 for TSP RH_{AM}. One filter showed an unexplained overall weight loss (TSP 24 19/07/98) and the result was therefore omitted from subsequent analysis.

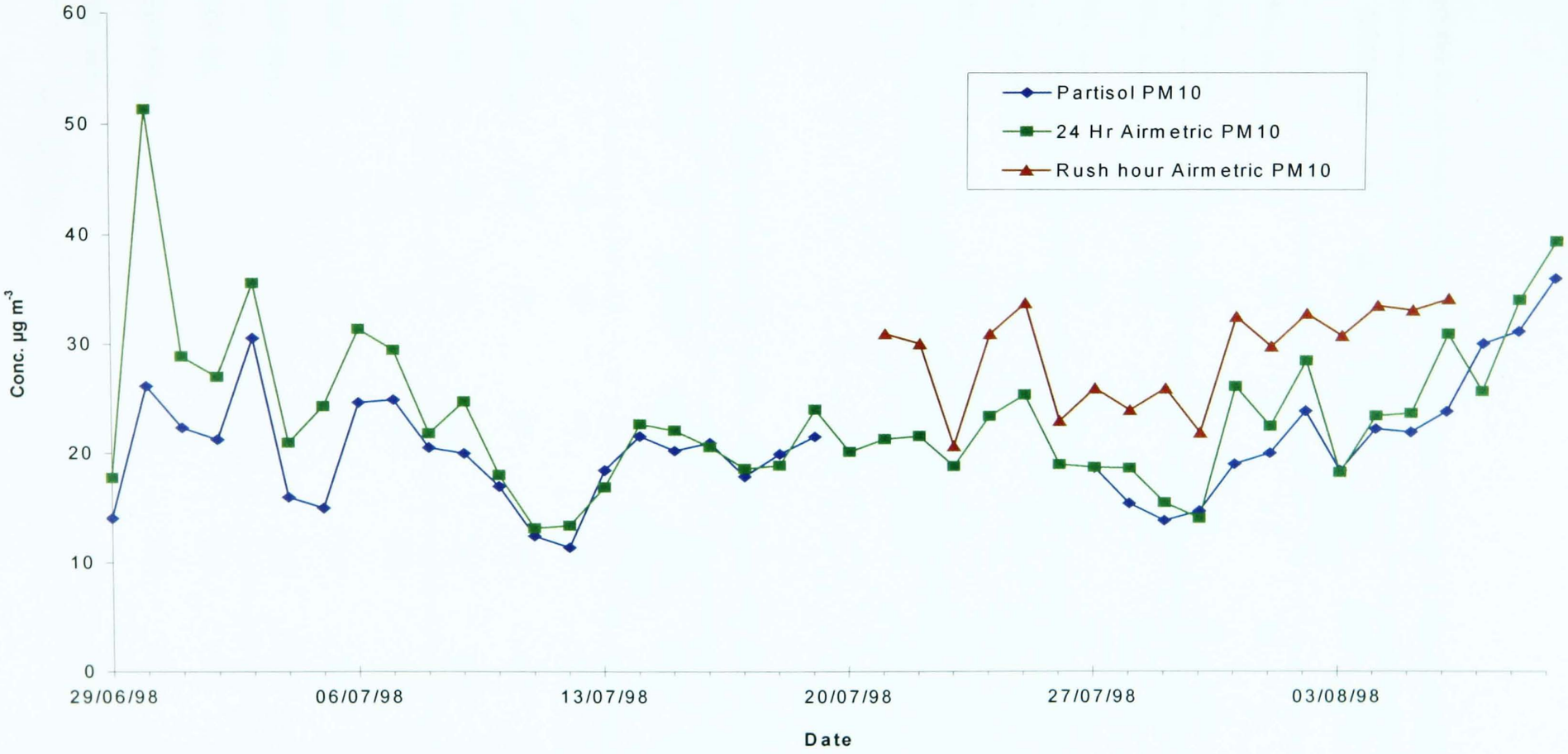


Figure 17: Time series plot for AirMetric PM_{10} data collected at Archway Road between 29/06/98 and 08/08/98. (Partisol PM_{10} included for comparison).

Table 9: Summary statistics for AirMetric PM_{10} data collected at Archway Road between 29/06/98 and 08/08/98.

AVERAGING PERIOD	SAMPLE	N*	MEAN#	MODE	STD ERROR	MAX	MIN	% PM_{10} PARTISOL
ALL	PM_{10} (Rush hrs)	17	34	29	1.2	34	21	162
DATA	PM_{10} (24 hr)	42	23	23	1.1	51	13	110
WEEK	PM_{10} (Rush hrs)	30	29	28	1.3	34	21	138
DAYS	PM_{10} (24 hr)	14	24	23	1.3	51	14	114
WEEK	PM_{10} (Rush hrs)	12	30	30	2.5	34	23	143
ENDS	PM_{10} (24 hr)	4	24	23	2.3	40	13	114

* Number of samples. All values in $\mu g\ m^{-3}$ #Arithmetic mean

Table 10: Summary statistics for TSP data collected at Archway Road between 29/06/98 and 08/08/98.

AVE PERIOD	FRACTION	N*	MEAN#	MODE	STD ERROR	MAX	MIN
ALL DATA	TSP 24	37	23	19	15	73	8
	TSP RH_{AM}	40	35	32	18	111	15
	TSP RH_{PM}	42	45	41	21	125	11
WEEK DAYS	TSP 24	28	22	18	2.5	47	8
	TSP RH_{AM}	29	33	32	1.9	61	20
	TSP RH_{PM}	30	47	42	4.0	125	11
WEEK ENDS	TSP 24	9	27	22	6.3	73	10
	TSP RH_{AM}	12	42	37	7.5	111	15
	TSP RH_{PM}	11	39	31	4.5	67	21

* Number of samples. All values in $\mu g\ m^{-3}$ #Arithmetic mean

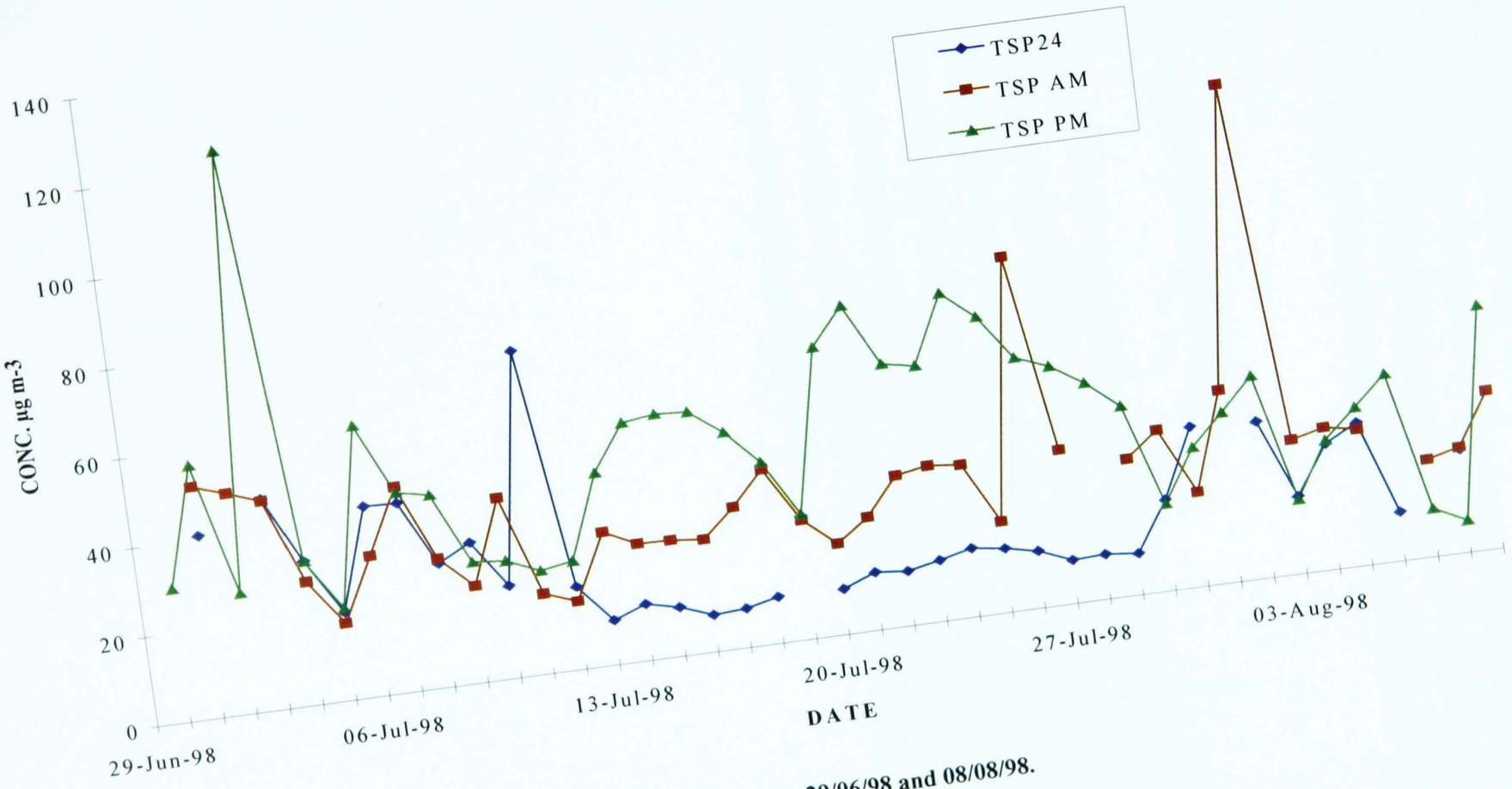


Figure 18: Time series for all TSP data collected at Archway Road between 29/06/98 and 08/08/98.

The summary statistics for TSP (Table 10) show that during the sampling period and during weekdays, the evening rush hour made a large contribution to overall 24-hour TSP concentrations, with high average concentrations in this period. Over the weekends, morning rush hours showed the highest concentrations. During the study those periods showing the highest concentrations were also the periods showing the most variance (indicated by the standard error), this reflects the typical variability of TSP levels, with some periods showing very high results as can be seen clearly in Figure 18.

8.4 Black Smoke (BS) Data

Black smoke data was collected as a 24-hour average. Four filters were contaminated (21 to 25/07/98) and, therefore, were omitted from the data analysis. This represents a data capture of 90%. Figure 16 shows the time series plot for BS, a similar trend can be observed in Figure 16 for Partisol PM_x data. The average BS concentration was found to be 22 $\mu g\ m^{-3}$ (see Table 11). However, the standard errors were relatively large and the data range relatively wide, which may suggest that this is not a good indicator of concentrations. The weekday concentrations showed a distinct elevation over weekend values that were markedly absent in PM_X values.

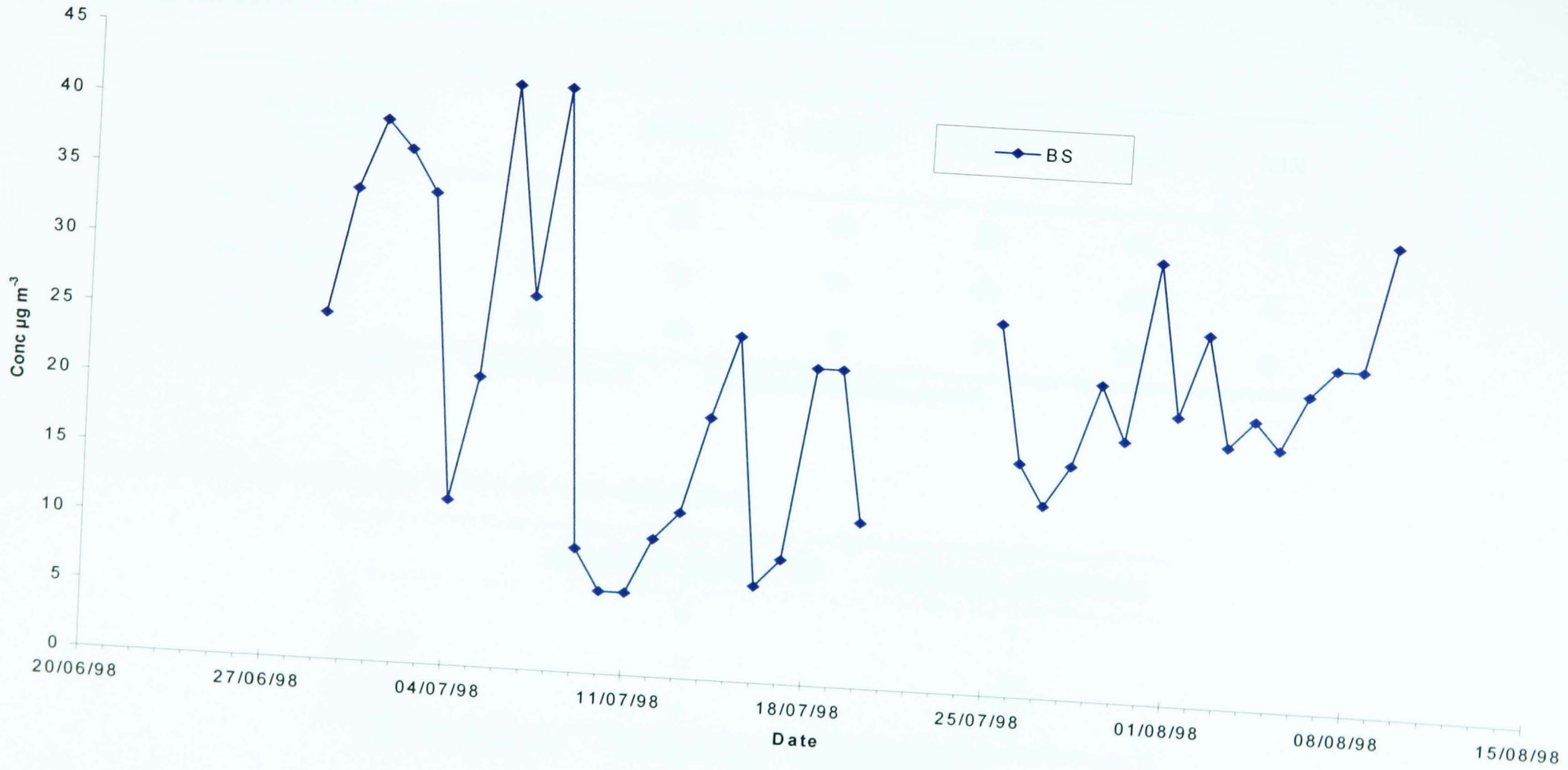


Figure 19: Black smoke; time series, data

Table 11: Summary statistics for black smoke data collected at Archway Road between 29/06/98 and 08/08/98.

AVERAGING PERIOD	N*	MEAN#	STDEV	MODE	MAX	MIN
ALL DATA	38	22	10	23	42	6
WEEK DAY	26	22	11	19	42	6
WEEK END	12	19	8	11	27	6

* Number of samples #Arithmetic mean All concentrations in µg m-3

Table 12: Summary statistics for weight change controls for Archway Road study.

	AIRMETRIC CONTROLS	PARTISOL CONTROLS
N*	8	7
MEAN#	20	11
STDEV	6	9

* Number of samples. #Arithmetic mean All values in µg

8.5 Controls

Controls were used to estimate the errors incurred through the handling, transportation and weighing of all filters for PM_x and TSP monitoring. The protocols for the handling of these filters were identical to those for their respective samples. Black Smoke method is a self-controlling method as the clean section of the filter is used to represent the blank reflectance. Therefore, any soiling in transit and use is accounted for in the final analysis. No controls were collected.

AirMetric filter controls were subject to more weight gain in their holders compared to the Partisol filter controls, as can be seen from Table 12. On two occasions substantial weight losses occurred with AirMetric filters, this was due to tearing in their holders and extra care was taken to avoid this during the study. The weight gains seen in Table 12 indicate an average gain of 2.78 $\mu g\ m^{-3}$ for the AirMetric and 0.46 $\mu g\ m^{-3}$ for the Partisol, these were assumed to represent a systematic error when analysing the results later.

The lower standard deviations for the AirMetric filters reflect a uniform weight gain across all controls. This was assumed to be due to different filter holder design. The AirMetric filters were totally enclosed in their holders and were therefore less exposed to contamination after their installation. Whereas, Partisol holders were open-faced, individual filters were therefore more exposed to possible weight-gains during transit. This would only affect certain filters, introducing higher variability to the mean weight changes of controls (and all other filters), this being reflected by a higher standard error.

For this study, it was considered that the comparisons between PM_{10} monitor performance was more accurately represented if errors due to filter weight losses and gains were not subtracted from the results. This is justified by the relatively large standard deviations for Partisol filters (i.e. weight gains seen on individual filters). It was considered that these gains were specific to individual filters in the case of the Partisol and were an integral aspect of the overall performance of the monitor. This is not in the case for the AirMetric, therefore, deduction from the Partisol data set has a different effect than in the case of the AirMetric.

9. DISCUSSION

9.1 Legislative Limits

PM_{10} levels recorded by both the Partisol and the AirMetric monitors were found to be below the UK Air Quality Standard of 50μg m^{-3} (a 24 hour running mean; National Air Quality Standards, NAQS (1998), recommended by EPAQS, EU, COMEAP and WHO). This is true with the exception of one occasion (AirMetric 24 hour PM_{10} 30/06/98) which was considered erroneous (see Figure 16).

The summary statistics for PM_{10} (see sections 8.1 and 8.2) showed that, throughout the monitoring period PM_{10} levels ranged between 68 and 38% lower than the 50μg m^{-3} NAQS limit (as a 24 hour average). On average, levels were found to be 42% of the limit. These levels are consistent with the comparative data obtained (see section 9.3.1) implying that the Archway Road area is relatively typical of London with respect to ambient PM_{10} pollution. However, as is noted later, monitors were placed at a high level and set back from the road. This study would have benefited from a road side or ground level PM_{10} monitor at the site for comparison data.

As the contributions of $PM_{2.5}$ and PM_1 to PM_{10} were found to be considerable, (see section 9.3.2) it may be worth considering that the legislative measures now in place in the UK will require updating to include legislation for finer fractions. It is known that these fractions result from anthroprogenic sources (in the absence of natural combustion sources) (QUARG 1995) and therefore represent a problem with the potential to be controlled through legislation. It is also understood that these fractions penetrate deeper into the lung and even show increased toxicity in the sub-micron-PM_1 range (COMEAP 1996). This study, other published work (i.e. Harrison *et al* 1997) and the monitoring undertaken via the Enhanced Urban Network (EUN) has demonstrated that $PM_{2.5}$ is a suitable fraction for both short and long term monitoring. This fraction represents a problem similar to PM_{10} in magnitude with possibly enhanced health implications, and therefore is highly relevant in respect to future legislation.

9.2 Comparison of PM_{10} Monitors

The reliability of the AirMetric sampler as a PM_{10} monitor was not reported in the literature review. It seemed important, therefore, to compare the AirMetric results with the Partisol PM_{10} results. Given that the Partisol is a USEPA reference method (having withstood extensive testing in the US) it seemed sensible to use the latter as the PM_{10} reference. it follows that throughout this chapter the Partisol results are assumed 'correct'.

Regression analysis for the AirMetric and Partisol PM_{10} data (Figure 20) gave the relationship

$$^{AirMetric}PM_{10} = (1.03 \times {}^{Partisol}PM_{10}) + 1.9\ \mu g\ m^{-3}$$

with an R^2 value of 0.79, i.e. the expression explains 79% of the data. This ignored the erroneous AirMetric data point mentioned earlier as it lay outside the 98th percentile of the data set. This indicates an error of 3% + 1.9 μg m^{-3} with respect to the AirMetric, representing an error of 4.4 μg m^{-3} for the maximum value of 51 μg m^{-3}. The systematic aspect of this error is the result of the weight gains seen on unexposed filters; section 8.5. The other 3% error is the result of the design tolerances of the AirMetric. The intersample variation may also be explained in part by the natural aspect of PM_{10}, biological particles of high mass and low AD may affect individual filters. This effect would not be seen in the finer fractions as $PM_{2.5}$ and lower are 99.9 % of anthroprogenic origin and can be assumed to be more evenly distributed in larger numbers (Wilson and Spengler 1996).

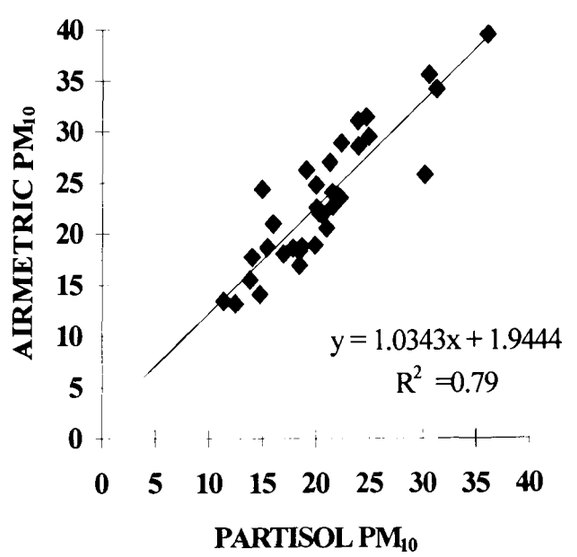


Figure 20: Regression analysis of Partisol monitored PM_{10} (24 hr) and AirMetric monitored PM_{10} (24 hr)

Figure 20 shows the strong correlation between the two PM_{10} samplers. It is concluded that the two monitors were measuring the same fraction with an acceptable degree of precision. In order to compare the two monitors further, regression analysis for both monitors against $PM_{2.5}$ were compared. The two expressions found were very similar:

$$PM_{2.5} = (1.2969 \times {}^{AirMetric}PM_{10}) + 3.336\ \mu g\ m^{-3} \quad \text{and}$$

$$PM_{2.5} = (1.3441 \times {}^{Partisol}PM_{10}) + 5.5493\ \mu g\ m^{-3}$$

This gives an error of 4.7% + 2.21 $\mu g\ m^{-3}$ for the AirMetric, which compares favourably with the error of 3% + 1.9 $\mu g\ m^{-3}$ based on the regression of Partisol and AirMetric PM_{10} data. This further strengthens the assumption that the AirMetric is a robust PM_{10} monitor.

9.3 Partisol and AirMetric PM_X Data

The Archway Partisol PM_{10} (being a USEPA standard method) data from this site was compared with several AUN sites (Department of the Environment, Transport and the Regions (DETR) web pages www.aea.com/airqual 1998). Four of these sites were roadside sites; Haringey: situated in North London, Camden: local to the study, Bloomsbury: situated in central London and Eltham: situated in South London. None of these sites showed exceedence of the NAQS limit for the duration of the study, despite being roadside sites. All sites showed similar trends suggesting that emissions (and therefore sources) are similar in all areas. Considering the roadside nature of these sites it is safe to assume that this source is traffic emissions.

9.3.1 PM_{10} 24 Hour Data and Comparisons

Summary statistics for comparative sites (Table 13) indicate that the PM_{10} monitored at the Archway Road site compares favourably with concentrations reported for Camden and Bloomsbury roadside sites with a little more variation in the data. Considering the location of the Archway Road site (5.1 m high and ≈11m from the centre of the road) this may suggest that the levels at the Archway Road site are relatively high for London, more detailed studies over long periods of time, possibly with road side measurements would be needed to investigate this Possibility.

Table 13: Summary statistics from study site and comparative site for the period 29/06/1999 to 08/08/1999.

SITE	ARCHWAY	HARINGEY	ELTHAM	CAMDEN	BLOOMSBURY	RURAL
N*	34	32	38	40	41	33
MEAN	21	18	15	21	21	10
STDEV	6	4	3	5	4	3

Conc. in $\mu g\ m^{-3}$ N* = no. of samples

It can be seen from Table 13 that average PM_{10} concentrations for London sites are between 5 and 11 $\mu g\ m^{-3}$ higher than the rural site. This suggests that 55% - 66% of the sources of PM_{10} at these sites are of local origin.

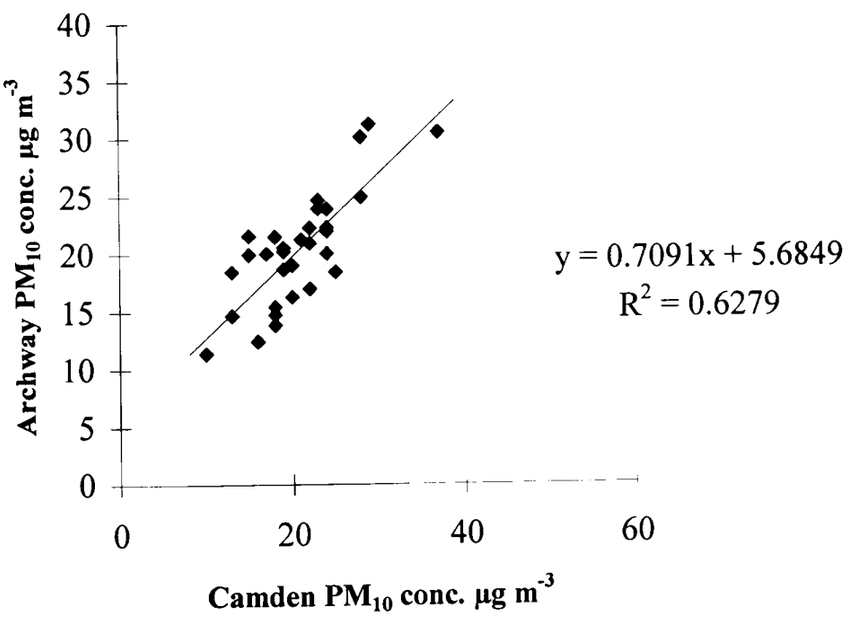


Figure 21: Regression analysis of Camden roadside PM_{10} and Archway PM_{10}

The regression analysis of Camden roadside PM_{10} and Archway PM_{10} showed that the two were reasonably correlated ($R^2 = 0.628$) and that Camden concentrations were marginally higher (see Figure 21). This was expected given the difference in the location of monitors. The monitor at Archway was situated at a height of 5.8 m and was set back from the road by 5.9 m (11.4 from the centre of the road). The monitor at Camden roadside is situated at an approximate height of 2m. This and the variations in traffic flows at both sites will have a

strong effect on monitored PM_{10} concentrations, as the more coarse and dense particles will tend to be removed from the atmosphere first. Also the TEOMS used at Camden and all AUN sites are known to underestimate in comparison to Partisol monitors due to loss of volatiles (ETI *Pers. comm.* 1998). A consistent undersample would not effect correlation patterns but may be important when considering average concentrations for regulatory purposes.

Figure 22 shows the time series plots for these sites and Archway. The interesting feature is that they all follow the same trends with Archway concentrations being comparatively high. However it does appear that there may be some elevation of concentrations at the Archway road site in comparison to the others in the last 3 days. This appears to be the beginning of a trend and as there is no data it cannot be commented on further.

It is evident from the time series plot (Figure 23), that PM_{10} levels have been low this year in comparison to previous years. At the beginning of the study they were at their lowest for four out of the five preceding years. This will result in lower than typical averages for the time period monitored. From this it is reasonable to presume that the values obtained at this site are either lower than typical levels or perhaps that that there is an ongoing downward trend in concentrations across London. The study would benefit from long term data sets for PM_{10} to help confirm or reject this suggestion.

Data for comparison were obtained from a rural AUN monitoring site for the same period as the study and for the previous year (time series: Figure 24). It is clear that PM_{10} levels at this site were also lower this year compared to last year. This may well indicate that meteorological conditions suited to dispersal prevailed throughout the period of this study. It is worth noting that rural concentrations were clearly much lower than those found at the urban sites, this being due to the lower density and number of sources contributing to local ambient concentrations.

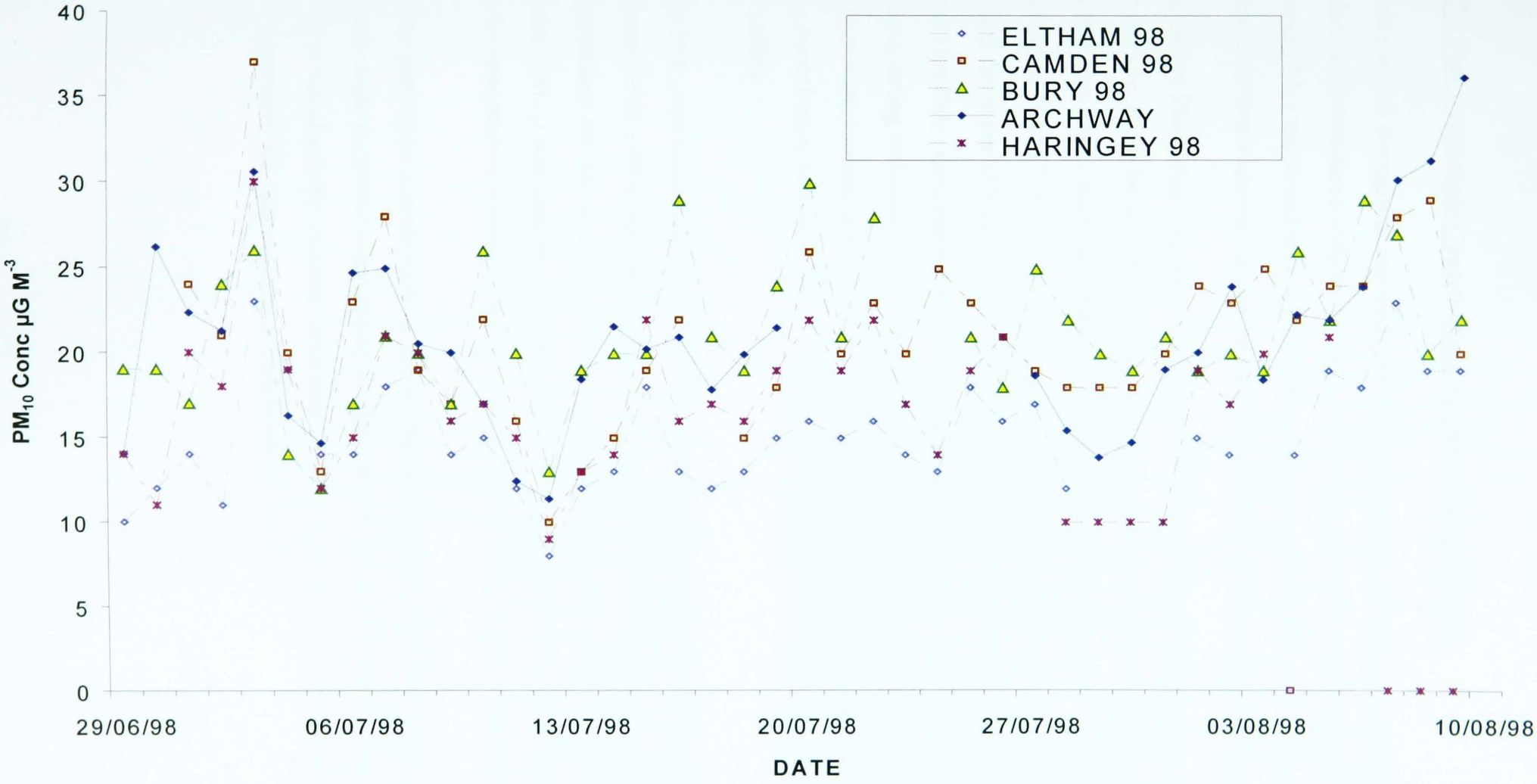


Figure 22: Comparison PM_{10} data from four AUN sites in London

9.3.2 Fine Particulate Contributions to PM_{10} Concentrations

At this site and throughout this study, $PM_{2.5}$ accounted for 76% of measured PM_{10} (based on Partisol data) compared with the findings of Harrison et *al* 1997 in Birmingham, where summer $PM_{2.5}$ was found to be 53% of PM_{10} (using co-located TEOMs) . The reasons for this difference weren't known but may be the result of a lack of the reuspended element of PM_{10}.

Comparison $PM_{2.5}$ data was obtained from the DETR web site (1998) from the Marylebone roadside site. It can be seen from Figure 25 that the two sites display a similar pattern and concentration range. Summary statistics showed an average of 13 $\mu g\ m^{-3}$ (with a standard deviation of 3$\mu g\ m^{-3}$, N= 34) for the Marylebone site. An average of 16 $\mu g\ m^{-3}$ (with a standard deviation of 5 $\mu g\ m^{-3}$, N = 33) was found for the Archway site, implying that on average the $PM_{2.5}$ concentrations are 23% higher at the Archway site. This is surprising and implies a strong influence from traffic, this being the only major combustion (and therefore fine particulate) source in the area. These high $PM_{2.5}$ levels may help to explain the large $PM_{2.5}$ contribution to overall PM_{10} if it is assumed to result from the main source in the area (i.e. traffic).

When $PM_{1.1}$ was monitored from 15/06/95 to 02/08/95 in Greenwich, London (Rickard and Ashmore 1996) a 48% contribution to PM_{10} was found. Summary statistics for PM_1 concentrations for this study show an average 62% contribution to PM_{10} at this site. This measure ($PM_{1.1}$) was used for comparison as no PM_1 data could be found in the literature, it must be remembered therefore, that this is not an exact ('like for like') comparison.

The fine particulate contributions to coarser fractions found in this study appear to be relatively high. As all the comparative studies considered were summer studies, removing any confusion introduced by seasonal variations, this lends strength to the assumption that local traffic represents the major source of particulate in this area.

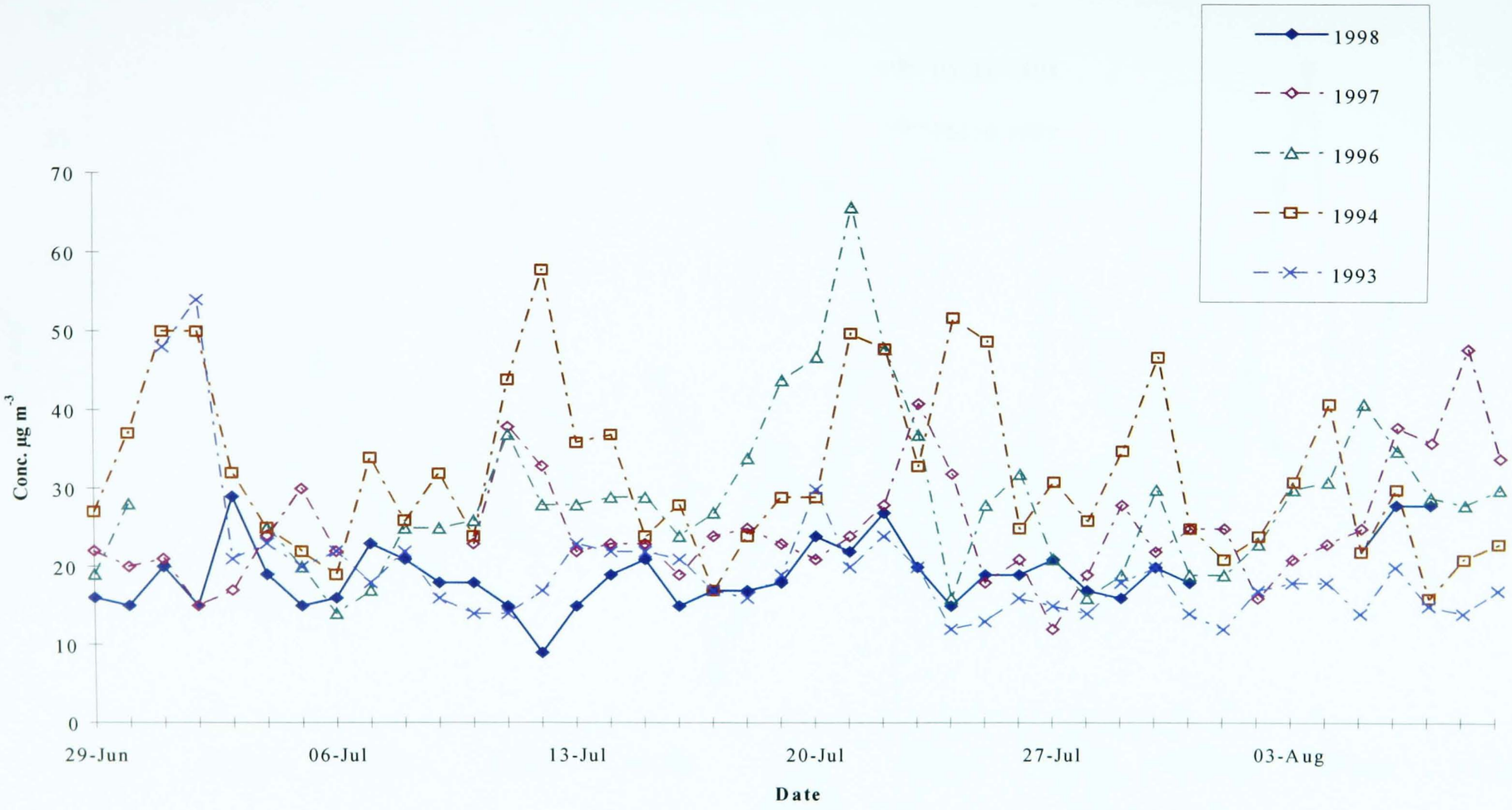


Figure 23: Time series plot of several years PM_{10} data from Marylebone AUN site (source DETR web pages).

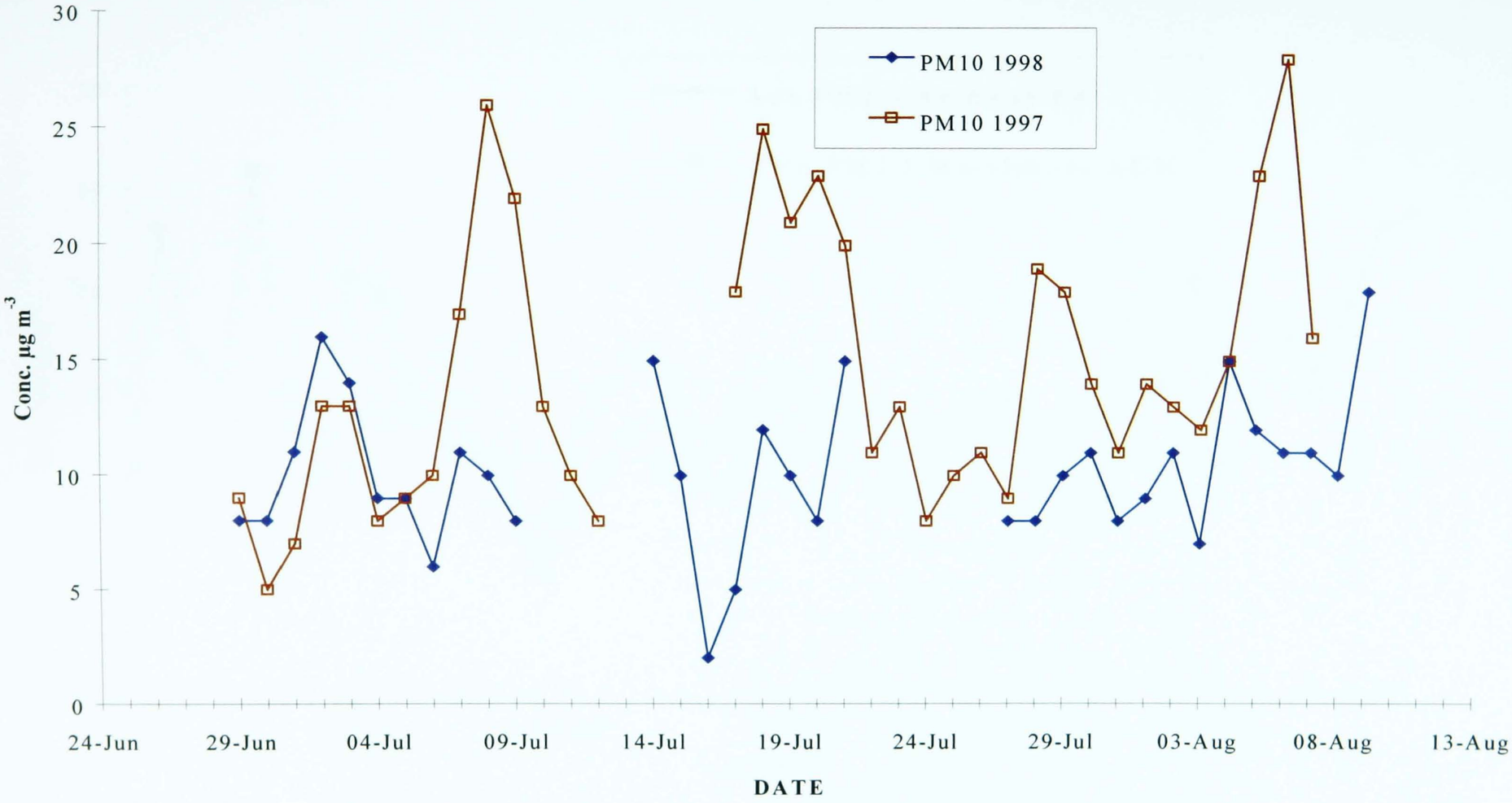


Figure 24: Time series plot of two years PM_{10} data from Narberth, a rural site

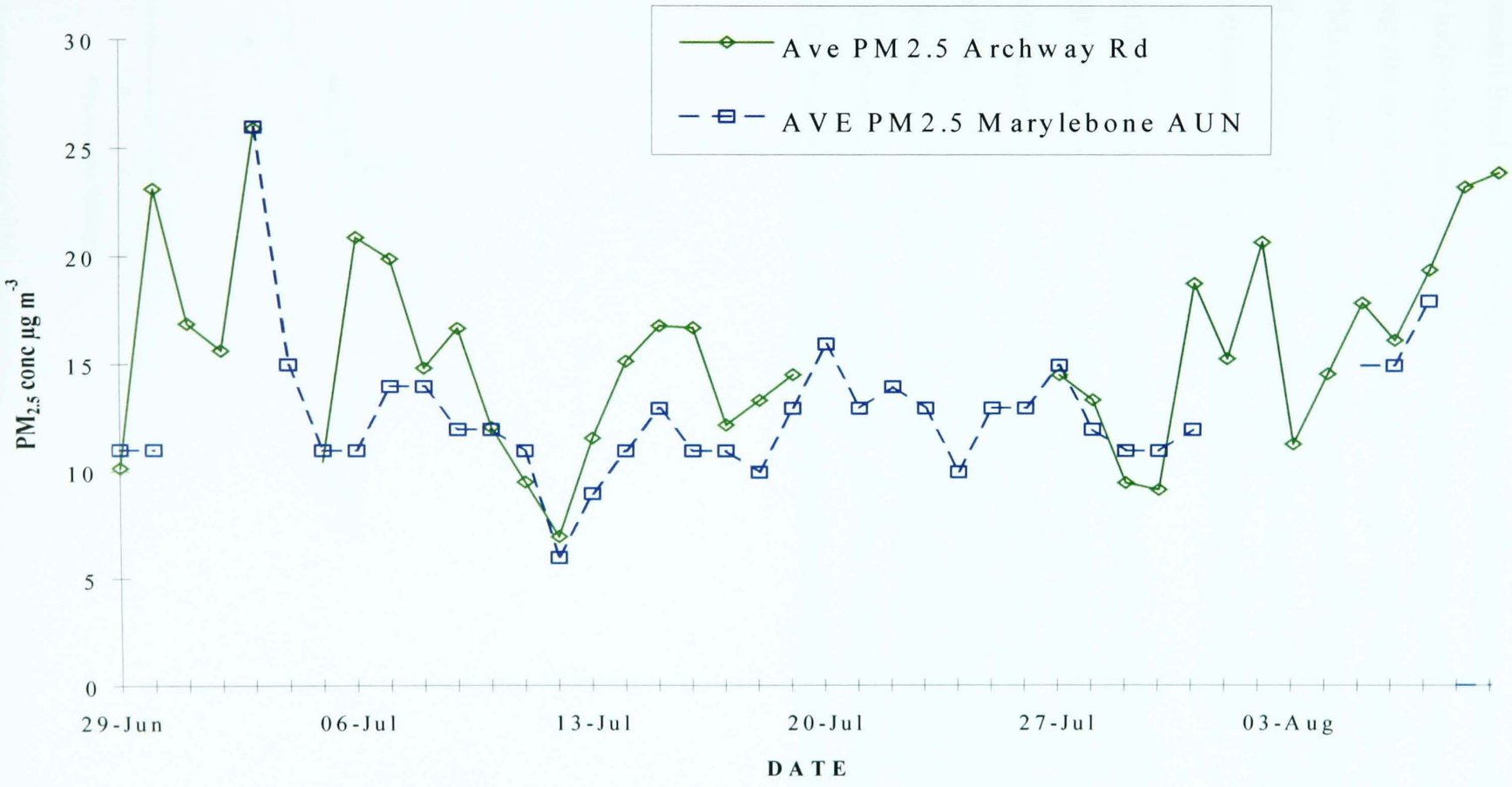


Figure 25: Time series plot of comparison $PM_{2.5}$ data from Marylebone AUN with Archway $PM_{2.5}$ (source DETR web pages)

9.3.2.1 $PM_{2.5}$ Concentrations at Archway Road and Comparisons

Regression analysis (Figure 26) was used to compare $PM_{2.5}$ concentrations at the Archway Road and Camden Road sites. The results showed a weak relationship between the two sites ($R^2 = 0.445$) indicating that although the two do show a similar pattern, this is not strong enough for one site to be used as a $PM_{2.5}$ predictor for the other. Given the evidence for the stability of $PM_{2.5}$ concentrations over large areas as reported by QUARG 1995, there is some suggestion of a substantial influence from local sources at one or both of these sites. Further, long-term monitoring and comparisons would be required to clarify this.

The effects of different monitors (TEOM and Partisol) and the variations in traffic flow at both sites will have a strong effect on monitored $PM_{2.5}$ concentrations. What is of interest is the overall similarities seen in the time series (Figure 25). This indicates that patterns for 24 hour average $PM_{2.5}$ concentrations are similar in different parts of London, this reflects the findings of QUARG (1995) and results from a combination of meteorological trends and city wide traffic flow patterns. This also indicates that there is a single, dominant source at the London sites, the rush hour PM_{10} concentrations strengthen the assumption that this is traffic related.

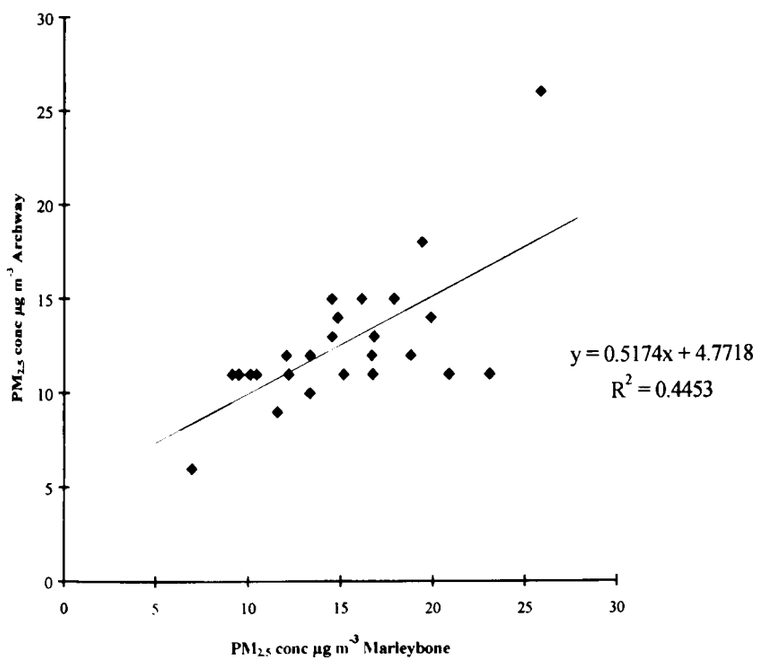


Figure 26: Regression analysis of $PM_{2.5}$ concentrations at Marylebone AUN site and Archway Road site

Again the major difference between the two sites is the positioning of the monitors. The monitor at Archway was placed at a height of 5.1 m and was set back from the road by 4.9 m (10.4 from the centre of the road) the monitor at Marylebone is at an approximate height of 2.0 m and is a few meters from the road.

Figure 27 and Figure 28 show the results of regression analysis of $PM_{2.5}$ against PM_{10} and PM_1 against PM_{10}, the R^2 value in both cases indicates a strong relationship between the finer fractions and PM_{10}. The relationship is a little stronger for $PM_{2.5}$ than for PM_{10}

($\boldsymbol{PM_{2.5} = (0.766 \times PM_{10}) - 0.357\ \mu g\ m^{-3}}$ $R^2 = 0.829$)

as opposed to that found for PM_{10} and PM_1

($\boldsymbol{PM_1 = (0.677 \times PM_{10}) - 0.507\ \mu g\ m^{-3}}$ $R^2 = 0.761$).

These relationships predict the ratio PM_{10}:$PM_{2.5}$:PM_1 to be 100:77:67, indicating that the contribution of PM_1 to PM_{10} to be stronger than when using their mean values as an estimate (giving the ratio 100:76:62). The intercept in both cases indicates the relevant background PM levels suggesting there is a small quantity of PM_x continuously suspended in the atmosphere (Dr Gorbunov *Pers. Comm.* Middlesex University 1999).

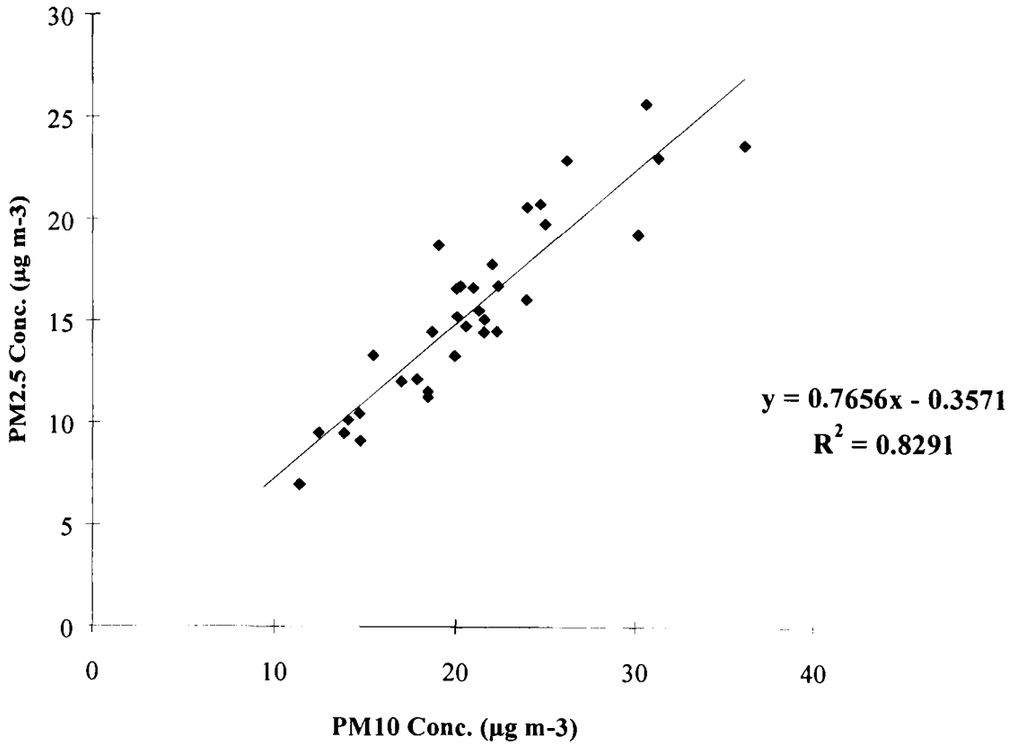


Figure 27: Regression analysis of PM_{10} V's $PM_{2.5}$

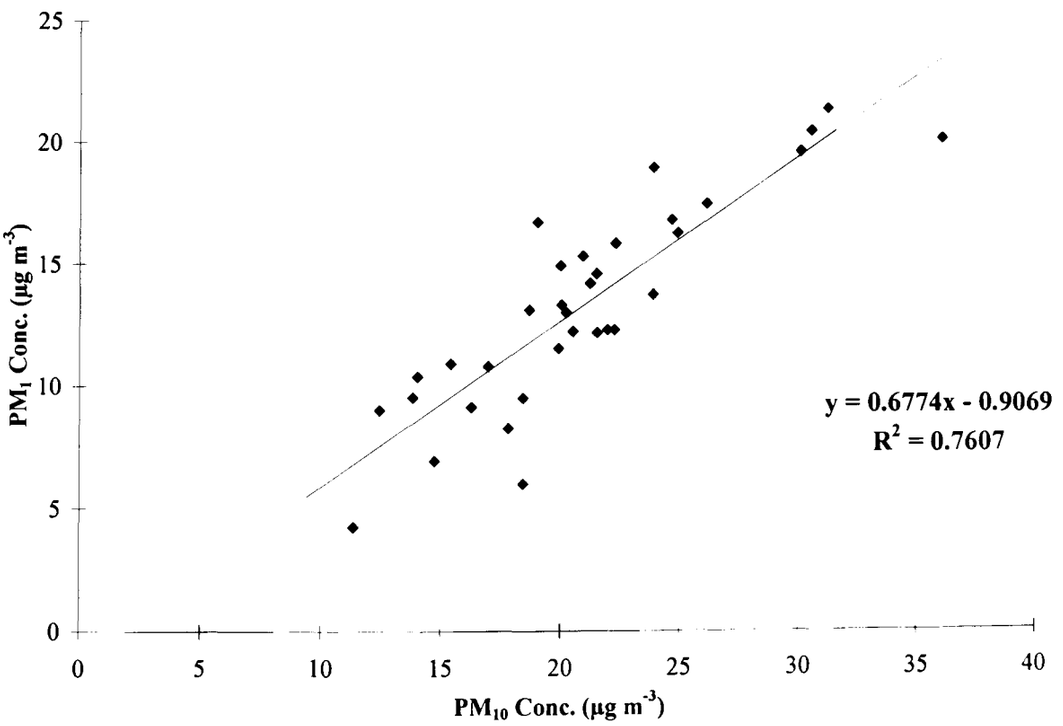


Figure 28: Regression analysis of PM_{10} V's PM_1

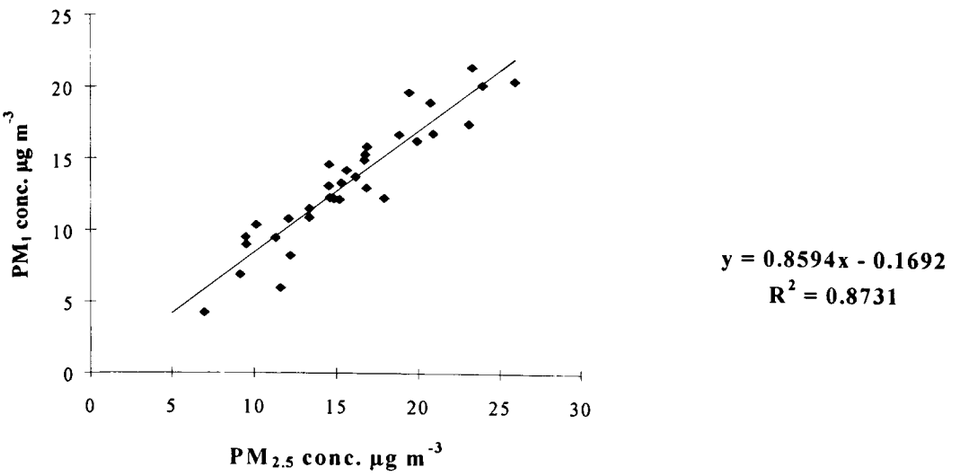


Figure 29: regression analysis for PM_1 and $PM_{2.5}$

Regression analysis of PM_1 against $PM_{2.5}$ (Figure 29) revealed that the two were highly correlated, $R^2 = 0.873$, their relationship being given by the expression:

$$PM_1 = (0.859 \times PM_{2.5}) - 0.169.$$

This indicates that PM_1 represents 86% of $PM_{2.5}$ (minus 0.17 µg m^{-3}), whilst the use of mean values gives this percentage as 81%. $PM_{1.1}$ was found to contribute to $PM_{2.1}$ by 85% in Greenwich, London (Rickard and Ashmore 1996), this indicates that the findings of this study are realistic and appear to support the findings of the regression analysis. However, it is important to remember that there is not a direct comparison available and that the Rickard and Ashmore study offered the nearest estimation available in the literature in the absence of co-located $PM_{2.5}$ and PM_1 studies.

9.3.3 Co-located$PM_{2.5}$ Errors for the Partisol

The two data set for $PM_{2.5}$ show very similar results and the summary statistics indicate that the Partisol has a high degree of precision (i.e. the results are highly reproducible). To analyse this assumption regression analysis was undertaken. The correlation coefficient (R^2) for the two sampling heads was found to be 0.8574 (see Figure 30), this omitted one data point which was clearly an outlier, after DETR practice to omit 98th percentile data, (*EPAQS 1998*).

The regression equation for the two co-located $PM_{2.5}$ data sets (SAT1 and SAT2) was found to be :-

$$SAT1 = (1.042 \times SAT2) - 0.7153.$$

This indicates that the two heads are collecting the same fraction (ideal situation: y = x or $PM_{2.5} = PM_{2.5}$). The intercept of -0.7153 indicates a systematic variation between the samples collected by the two $PM_{2.5}$ heads. It can be seen that one data point is having a strong influence on the regression (x=18, y=11). Removal of this point gave a new equation of:

$$SAT1 = (1.0653 \times SAT2) - 0.864$$

with an R^2 value of 0.9172. This indicates a similar, but negligible, systematic discrepancy and a very high degree of precision, errors being introduced through the handling and weighing of filters. Variations in collected concentrations could, in theory be a result of the different air being collected by each station, coupled with the fact that this study was undertaken within an urban street canyon (where micro climatic events are enhanced) this may appear to be the case. However, given that there was an apparently systematic error and a high degree of precision in the results, given the proximity of the two stations (< 1m apart), such microclimate variations were considered irrelevant for the sake of simplicity. Alternatively there may be small variations in inlet characteristics and or feed-lines to the filters which result in small variations. Variation from the ideal case (y = x) suggests a 4-6.5% error in addition to the systematic error, these represent an overall error of between 0.38 and 0.83 $\mu g\ m^{-3}$ in the case of the results obtained within this study. This level of error is small in comparison to the background level and gives confidence in the Partisol as being a precision instrument, which is producing dependable results.

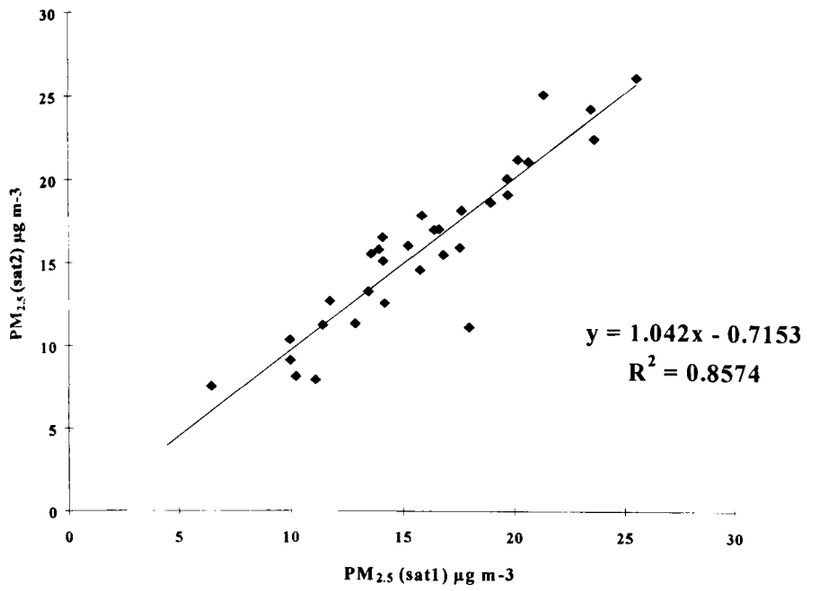


Figure 30: Correlation between the two $PM_{2.5}$ heads on the Partisol.

9.4 Rush Hour Data from AirMetric PM_{10} and TSP Monitors

Rush hour data for both TSP and AirMetric PM_{10} were found to be higher than the 24 hour running averages. This suggests that traffic is a major influence on particulate pollution at the Archway Road site. Combined rush hour data for PM_{10} was found to be on average 20% in excess of 24 hour data. TSP was found to average 52% higher during morning rush hours and 95% higher during evening rush hours than 24-hour averages. This was found to be 50% and 113% respectively over weekdays and 55% higher during morning rush hours and 32% lower during evening rush hour at weekends. This reflects the different traffic patterns during the week depending on commercial, social and working habits (discounting any variability in TSP due to other influences such as wind and rain).

9.4.1 PM_{10} Rush Hour Data

Regression analysis of rush hour and 24 hour AirMetric PM_{10} samples (Figure 31) suggests a relationship at this site as indicated by the R^2 value of 0.6326. The expression found was

$$24\ hour\ PM_{10} = (rush\ hour\ PM_{10} \times 0.6961) + 1.1844\ \mu g\ m^{-3}.$$

This implies that the 24 hour average is 70% of the rush hour average (+1.2 µg m^{-3}, giving a value of 73.56% at a rush hour concentration of 30µg m^{-3}). However, this only explains 63% of the data and is an over simplification. At very low rush hour concentrations (i.e. below 4 µg m^{-3}) this model predicts 24-hour concentrations to be in excess of rush hour concentrations, which never occurs, this simply serves to indicate the limitations of this

model. It does suggest that rush hour traffic may contribute to the overall 24 hour averages for the day and may imply that busy rush hours predict busy days with respect to traffic. It also suggests that a non-linear fit may be more relevant to this analysis.

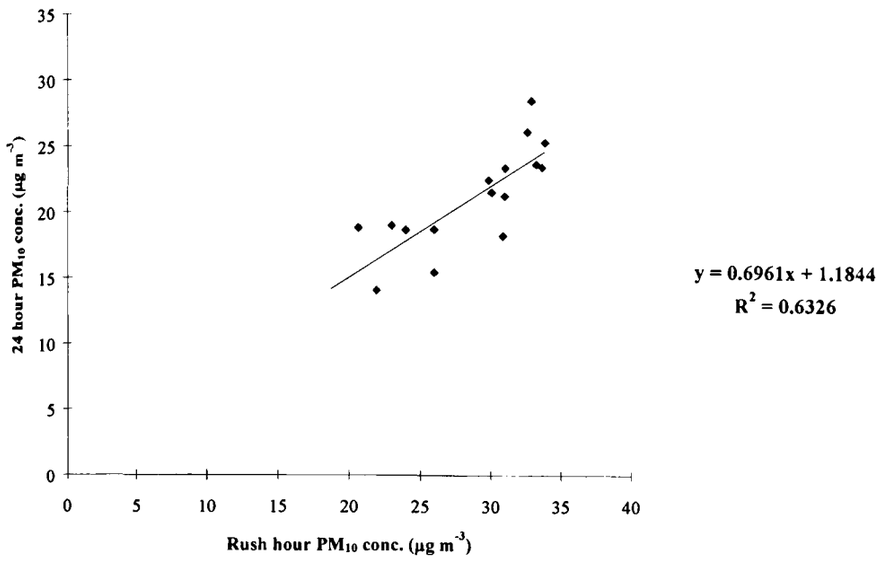


Figure 31: Regression analysis for 24 hour and rush hour PM_{10} AirMetric data

Weekday rush hour produced a 20% increase in PM_{10} compared to 24-hour averages throughout the study. At weekends this produced a 25% increase. These ratios were stable, which probably reflects the more stable nature of the fine particulates in the atmosphere (in comparison to the coarse fractions), and their increased residence time. Also, both rush hours were collected on one filter per day meaning changes in morning and evening driving patterns are not evident. Finally, it is well documented that particulate concentrations display diurnal variations (Harrison *et al* 1996, QUARG 1993, QUARG 1996), therefore some elevation of concentrations would be expected between the hours of 5 AM and 10 PM.

9.4.2 TSP Rush Hour Data

The TSP time series indicates that 24-hour TSP levels were found to be lower than rush hour levels, with morning rush hours generally giving the highest results. This may be a result of fixed four hour sampling periods for rush hours which are more flexible in timing and duration, especially in the evenings. Typically large fluctuations are evident, especially during the rush hour periods. TSP is more influenced by wind speed and rainfall than the finer fractions. Events such as these make average values less valuable as indicators of typical

values. The values obtained at the Archway Road site, when compared with the findings of Williams *et al* (1995), are low. Williams *et al* found concentrations as high as 130 μg m^{-3}, ranging upwards from 34 μg m^{-3}, the lower values being found in residential areas. However, similarly reduced values were found for PM_{10}.

The major differences between the two studies were positioning of monitors (the monitors were identical in both studies) and time of year. The monitors used by Williams *et al* (1995) were reported at 2.0 m above the ground on a mobile monitoring laboratory where as the monitors used for this study were at a height of 5.1 m and set 4.9 m back from the road. This impacts more on values for TSP than the finer fractions as the resuspended element is especially large and may be partially removed (via scavenging and fallout) before reaching the monitor. Given the size of particulate being considered for this argument, this would be expected to have a significant effect on sample mass. The study undertaken by Williams *et al* was during April 1991 as opposed to July and August for this study, given that April is a typically wet month the significance of the differences between concentrations found in these studies should be viewed with caution.

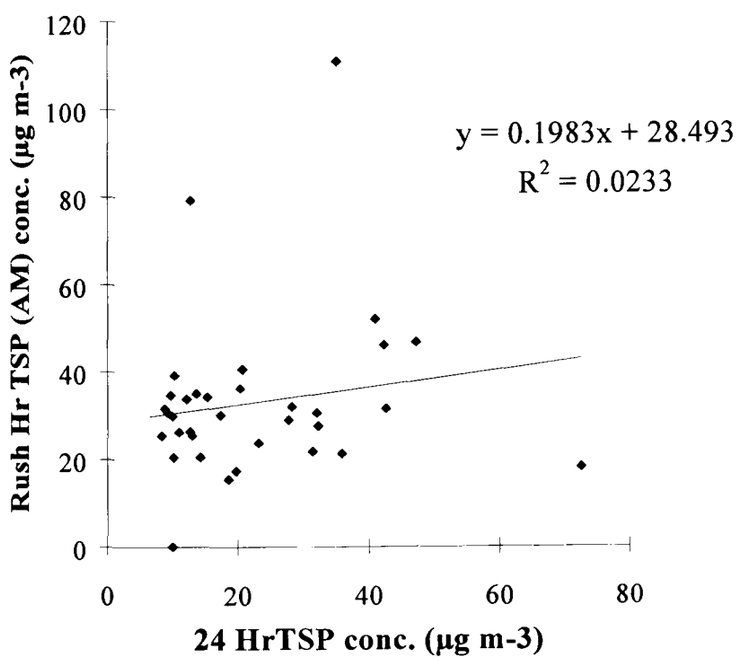


Figure 32: Correlation between 24 hour TSP concentrations (TSP24) and morning rush hour TSP concentrations (TSP RH_{AM}).

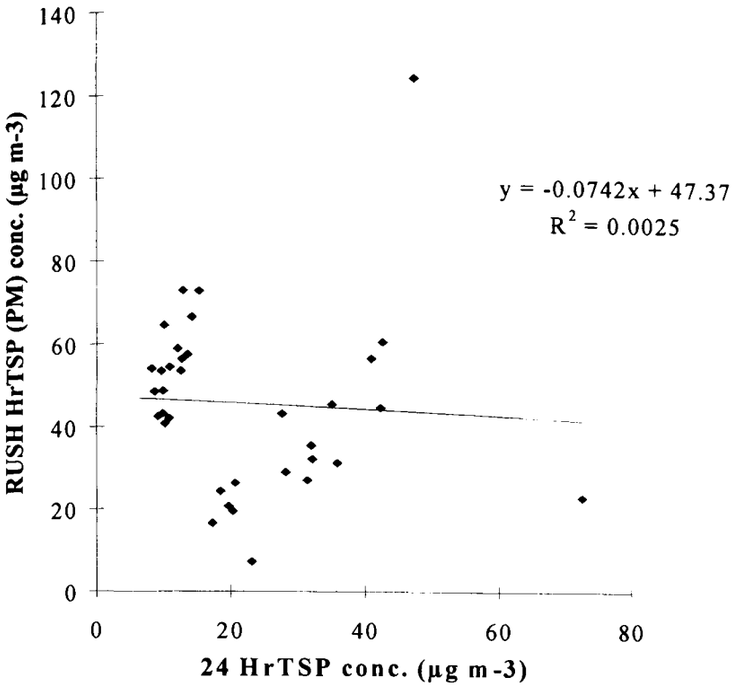


Figure 33: Correlation between 24 hour TSP concentrations (TSP24) and evening rush hour TSP concentrations (TSP RH_{PM}).

Regression analysis of rush hours and 24 hour concentrations were undertaken (see Figure 32 and Figure 33). No significant statistical relationships were found between rush hour concentrations and 24-hour concentrations. However, there may be a visual indication of a weak trend linking morning rush hour concentrations and 24 hour concentrations for TSP, with the reverse for evening rush hours. It would be more appropriate to break PM_{10} rush hour monitoring into RH_{AM} and RH_{PM} samples and run comparisons with 24 hour data as this fraction is more stable than TSP.

It is also clear from the pattern of the data that there are two apparent sub-sets within the main data set – indicating two subsets in the data (see Figure 33). Why this is the case is not clear, but may be the result of different meteorological conditions i.e. those taken on wet and dry, still and windy or combinations of these. It may be that the coincidence of rain with the evening rush-hour period would suppress the results for that sample on an otherwise dry day with high 24-hour concentrations. This combined with the reverse coincidence could result in two sub-sets separating. More data would possibly cause the two sub-sets to close up and be less distinct, more detailed meteorological information would allow for more detailed interpretation of this phenomenon and is worthy of further study.

9.5 BS Data

BS levels observed at this site were similar to those found by Williams *et al* (1995). With the exception of one extreme case which may well have been close to a bus station and depot: Wood Green commercial site mean BS = 70 $\mu g\ m^{-3}$ (Williams *et al* 1995). During the PEACE study Hoek *et al* (1997) reported BS levels between 3 and 99 $\mu g\ m^{-3}$ at a range of urban and rural locations across Europe, with the highest levels being found in Athens and the lowest in Scandinavia.

The fact that such high BS levels in comparison to PM_{10} were recorded at Archway Road is the result of out dated calibration tables. These were designed in the fifties and sixties to convert a different aerosol that was highly influenced by coal smoke. Occasions where this has occurred will probably be a result of a high proportion of diesel vehicles in the area on those days. This may be reflected in the distinct drop in week end values compared to week day values (see Table 11), with there being presumably more commercial diesel vehicles and buses operating on week days (week end averages being diluted by reduced Sunday traffic density).

9.6 Regression Analysis of all Fractions

To investigate all possible relationships, regression analysis was carried out using all possible combinations of the fractions measured as 24-hour averages. The results can be found in Table 14. From this table, it is clear that TSP had no strong relationships with any of the other fractions the strongest relationship giving an R^2 value of 0.1056. This is as would be expected, TSP being influenced by a great many environmental and anthroprogenic factors including wind speed and direction, rain fall and local emissions for example. The coefficient obtained by the co-located $PM_{2.5}$ samplers (where the theoretical value would be expected to be 0.1) can be used to indicate the limitations of the study. The variation being due to the cumulative errors within the entire sampling and analysis procedures.

Table 14: Regression coefficients (R^2) for all fractions monitored as 24 hour averages

	TSP	BS	$^{A}PM_{10}$	PM_{10}	$PM_{2.5}$	PM_1
TSP		0.098	0.0496	0.0467	0.0649	0.1056
BS			0.3411	0.2859	0.3201	0.3319
$^{A}PM_{10}$				0.79	0.8195	0.7751
PM_{10}					0.8226	0.7552
$PM_{2.5}$					* 0.8574	0.8731

^{A} AirMetric values *Co-locatedsamples

BS showed a weak relationship with all PM fractions of around $R^2 = 0.31$. This probably reflects the fact that the main source of dark (non-reflective) material is traffic emissions which are also the major source of the PM fractions (QUARG 1995). The low correlation coefficients may reflect the fact that the conversion tables are outdated, the nature of the aerosol having changed considerably since their construction, therefore the light absorption to mass ratio of a given sample has changed.

PM_{10} correlated well with the two finer fractions, slightly better with $PM_{2.5}$ than for PM_1 as these two fractions are more similar. Average $PM_{2.5}$ correlated better with PM_1 than the two co-located $PM_{2.5}$ samples, this probably reflects short term differences in levels between the two $PM_{2.5}$ sampling periods (a cycle of 5 minute samples across 4 heads over 24 hours) and errors due to gains and losses in the process of transportation and weighing. Average $PM_{2.5}$ may have smoothed out some of these errors and resulted in slightly better correlations between this and the other PM fractions.

The strongest correlation was between collocated $PM_{2.5}$, $PM_{2.5}$ and PM_1. This was expected as this is the size range around which there is a natural dip in the 'typical' mass versus particle numbers modal distribution. This is the point where particle numbers are naturally low, the nucleation and accumulation modes generally occurring in the sub-micron range and the coarse mode being above, both tending to have distinct and divergent sources, generating particles of distinctly different sizes (QUARG 1995 and others).

10.

CONCLUSIONS

From the study the following conclusions can be made:-

- PM_{10} 24-hour mean concentrations were found to be 21 $\mu g\ m^{-3}$. The respective mode value was found to be 20 $\mu g\ m^{-3}$.

- PM_{10} 24-hour mean concentrations were found to be consistently lower than the NAQS limit.

- $PM_{2.5}$ 24-hour mean concentrations were found to be 16 $\mu g\ m^{-3}$. The respective mode value was found to be 15 $\mu g\ m^{-3}$.

- PM_1 24-hour mean concentrations were found to be 13 $\mu g\ m^{-3}$. The respective mode value was found to be 13 $\mu g\ m^{-3}$.

- Weekend 24-hour averages were found to be identical for PM_{10} and slightly diminished for $PM_{2.5}$ and PM_1, in comparison to 24-hour averages for weekdays.

- AirMetric MiniVol PM_{10} concentrations were found to be consistently higher than ($\approx$110%) Partisol (USEPA standard method) concentrations, 24-hour average being found to be 23 $\mu g\ m^{-3}$. The respective mode value was found to be 23 $\mu g\ m^{-3}$.

- Rush hour PM_{10} concentrations were found to be consistently higher than 24-hour concentrations.

- When compared on the basis of means the AirMetric showed a 10% oversample compared to the Partisol as standard.

- When compared on the basis of regression analysis of both 24-hour PM_{10} data sets a 3% + 1.9 $\mu g\ m^{-3}$ error was found for the AirMetric.

- When compared using regression analysis of both 24-hour PM_{10} data sets against $PM_{2.5}$, a 4.7% + 2.21 $\mu g\ m^{-3}$ error was found for the AirMetric.

- The fixed (systematic) component of the above errors were partially explained by the analysis of controls which found a more erratic and larger weight gain for AirMetric filters throughout the protocol in comparison to Partisol filters.

- TSP 24-hour mean concentrations were found to be 23 $\mu g\ m^{-3}$, RH_{AM} – 35 $\mu g\ m^{-3}$, RH_{PM} – 45 $\mu g\ m^{-3}$. The respective modal values were found to be 19 $\mu g\ m^{-3}$ 32 $\mu g\ m^{-3}$ and 41 $\mu g\ m^{-3}$

- Weekend TSP concentrations were found to be slightly higher than weekdays.

- The weekday pattern; higher RH_{PM} TSP concentrations than RH_{AM}, was found to be the reverse at weekends.

- Black Smoke 24-hour concentrations were found to average 22 $\mu g\ m^{-3}$.

- Weekend concentrations were found to be slightly lower than weekdays for BS.

- Archway PM_{10} concentrations were found to be comparable to other London Roadside sites whilst being higher than urban background, suburban and rural sites.

- Regression analysis of co-located Partisol $PM_{2.5}$ showed the Partisol to be a precision monitor (R^2= 0.92).

- All other fractions were analysed using regression analysis, this showed strong relationships between PM_x fractions and all others to be statistically weak.

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Glossary of Terms

Accumulation mode

The fraction of airborne particulates between approximately 0.1-2.0 μm AD generally the result of nucleation mode particles accumulating mass.

Aerodynamic diameter (AD)

The diameter particle would have if it were spherical, have a unit density of 1g cm^{-3} and have the same sedimentation rate.

Aerosol

A collection of particles suspended in the atmosphere.

Black smoke

Non-reflective (dark) particulates associated with the Black Smoke method.

Coarse mode

Generally those particles greater than about 2 μm AD. Often of mechanical origin.

Fine particulate

Particles smaller than about 2 μm in AD. Including the nucleation and accumulation modes.

Hygroscopic growth

Growth of particles due uptake of moisture in the atmosphere.

Inhalable particles

Particles which may be breathed in or inhaled.

Mass concentration

Particle concentration expressed as mass per unit volume: i.e. $\mu g\ m^{-3}$.

Nucleation mode

The aerosol fraction below around 100nm.

PM1

Particulate mater <1 μm AD. Or that fraction collected using a size selective preseperator with a 50% efficiency cut-off point at 1 μm AD.

PM2.5

Particulate mater <2.5 μm AD. Or that fraction collected using a size selective preseperator with a 50% efficiency cut-off point at 2.5 μm AD.

PM10

Particulate mater <10 μm AD. Or that fraction collected using a size selective preseperator with a 50% efficiency cut-off point at 10 μm AD.

Relative humidity (RH)

Actual vapour pressure/saturated vapour pressure expressed as a percentage.

Respirable particles

Particles which penetrate to the uncilliated parts of the lung.

TEOM

Tapered Element Oscillating Microbalance, an instrument for near real-time measurements of aerosols.

Thoracic particles

The fraction of particles penetrating beyond the nasopharynx and larynx.

Total suspended particles (TSP)

The fraction of an aerosol collected on an open-faced filter, generally gravimetrically determined.

Ultrafine particles

Particles less than 50 nm in AD (some use 100 AD).

A Pilot Study in Preparation for Particulate Characterisation at a Site on the Archway Road London.

The use of the Partisol 2000 automatic sampler, AirMetrics minivol portable sampler.

MAURICE MOORE

Towards the requirements for the completion of the qualification:
BPhil in Particulate air pollution.

APRIL 1998

Work undertaken at UPRC Middlesex University, Bounds Green, Bounds Green Road, LONDON, N11 2NQ

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ABSTRACT

The Partisol 2000 Starnet air sampling system and AirMetrics portable air sampler were tested on the roof of Middlesex University, North London. Samples of PM_{10}, $PM_{2.5}$ and PM_1 were taken using the Partisol 2000, the AirMetrics samples for PM_{10}. The most suitable filter type was assessed from several samples of both cellulose nitrate and Teflon filters, with particular reference to their cost and susceptibility to weight changes induced by moisture or static. The Teflon filters proved to be the more suitable and were used to assess the suitability of various sampling periods for the samplers. The resulting samples were digested using the nitric/perchloric method, and were subsequently analysed for, using Inductively Coupled Plasma/Atomic Emission Spectrometry (ICPAES Perkin Elmer Model Plasma 40 Spectrometer), attention was paid to the relevant standards matrix for calibration.

AIMS

The aims of this pilot study were to:

- Develop an understanding of the procedures involved in the weighing of filters (loaded and unloaded).
- Develop an understanding of the Partisol 2000 and AirMetrics samplers.
- Overcome any problems arising from the above procedure.
- Determine the most suitable filters for the main study.
- Gain a working knowledge of the sampling equipment.
- Ensure that the sampling periods proposed for the main study will provide measurable samples.
- Undertake a simple analysis of metals present in the samples collected.

The site for the pilot study was the Northwest side of Middlesex University roof; Bounds Green Campus, Bounds Green Road, London N11 (see plate 1). This part of the roof is approximately 15m above street level and within 30m of traffic lights where the North Circular (A404) crosses Bounds Green Road. Traffic volumes there are high (typically around 35 000 vehicles per day in August 1992; Haringey Council, *Pers. Comm* 1998) and can be estimated as being similar to those of the main study site; Archway Road, North London (A1) a busy high street condensed from dual carriageway in both directions.

Figure 34: The Partisol 2000 and AirMetric sampling equipment on the roof at Middlesex University, North London, (information being downloaded from Partisol).

Weighing and Sampling

The author procured test filters from Whatmans, Millipore and Gelmans Scientific; the first two companies provided a variety of 47 mm diameter, cellulose nitrate filters and the latter provided a variety of 47 mm diameter, Teflon filters.

The cellulose membrane filters were identical in construction and had a nominal pore sizes of 0.2, 0.45 and 0.8 μm. These filters were of the tortuous path type.

The Teflon filters were of two types: a PTFE mesh, pore size 2.0 μm, with PNP support ring and two PTFE mesh, pore size 1.0 and 0.5 μm, with structural PNP support.

- The filters were conditioned for 24 hours in the clean room facilities at Middlesex University and then weighed twice at 24 hour intervals before sampling to determine the blank mass.
- The average of the two (given an accuracy of ± 3.0 μg), relative humidity and temperature were recorded at each stage.
- A change of ± 5% relative humidity or ± 5°C in clean room environment was considered unacceptable as studies have shown the distinct effects of humidity on particulates, weighing was not undertaken if these criteria were not met.
- The filters were then exposed.
- The samples were then conditioned in the clean room for 24 hours and weighed twice at a minimum of 24-hour intervals as above.

The particulate matter (PM) mass (M_{PM}) was determined by taking the clean filter mass (FM_C) from the loaded filter mass (FM_L) (equation 1):

$$M_{PM} = FM_L - FM_C \qquad \text{....Equation 1.}$$

This mass was converted to mass per unit volume by dividing M_{PM} by the volume of air that had passed through the filter whilst sampling (V_{STD}) (equation 2):

$$M_{PM} = \frac{FM_L - FM_C}{V_{STD}} \qquad \text{....Equation 2.}$$

All weights were be reported as μg and volumes as m^3, therefore, the results produced are expressed as μg m^{-3}.

Both AirMetrics™ (minivol) and Partisol 2000™ samplers were used in this study, the latter was fitted with PM_{10}, $PM_{2.5}$ and PM_1 heads, the former with PM_{10}.

As previously described for the main study, the Partisol 2000 (PS) consists of a stand-alone hub with three optional satellites (consisting of sampling head and filter holder), the PS runs on mains power only and samples at a rate of 16.7 L min^{-1}. The satellites are connected, via an air line, to the hub at a distance of around 3m and are switched using solenoids in the hub. The hub controls the system with user defined programmes, allowing for a maximum of 8 samples a day (on 4 filters), the sampling periods can be sequenced across two or more sampling stations given that the sampling periods are identical.

As per the main study, the AirMetrics (APS) consists of a sampling unit with a quick-fit PM_{10} head. The sampler samples at a rate of 5 L min^{-1} and uses a rechargeable battery (24hr capacity) for power. The sampler is programmable allowing for a maximum of 6 sampling runs to be run on one filter (this being restricted by the life of the battery).

For this pilot study the samplers were run for varying time periods, ranging from 24 hours to 4 hours (see table 3), and the resultant samples were then quantified.

Sample Digestion for Metals Analysis

The samples were digested using the nitric perchloric method (Richmond, 1993) for subsequent analysis of metal content, the digestion procedure was as follows:

- In a back washing fume cupboard, the filters were carefully placed in Teflon lined, acid washed beaker and covered with 10-20mL of a 9:1 ratio of 70% aqueous nitric acid (HNO_3) and 70% aqueous perchloric acid (HClO).
- The filters were agitated with an acid washed glass rod for 1 minute.
- The rod was washed in double distilled, deionised water and dried between samples.
- The samples were placed on a heated sand bath (40-80^{O}C) and allowed to evaporate to dryness.
- The fume cupboard was back washed.
- The residue was re-constituted using 5 mL of 10% HNO_3 .
- The reconstituted solution was filtered using a Whatmans no. 42 filter into a 10 mL volumetric flask.
- The beaker, funnel and filter were rinsed for residual metals using 5mL 10% HNO_3 .
- The volume was made up to 10mL using 10% HNO_3 .
- A blank was generated using a clean filter following the above procedure.

Metals Analysis

The prepared samples were analysed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP/AES) using a Perkin Elmer model Plasma 40 Spectrometer.

- The ICP was calibrated using a blank generated during digestion (as zero) and 1000ppm metals standards.
- The samples were analysed using three replicates.
- Samples were tested for Cd, Cr, Cu, Ni, Pb and Zn.

The results of the initial weighing of cellulose nitrate filters are shown in Table 1.

Metals in the atmosphere are reported as mass per unit volume i.e. ng m^{-3}, this is calculated as shown in equation 3:

$$M_{ngm}{}^{-3} = \frac{Mppm \times 10}{Vstd} \qquad \text{.....Equation 3.}$$

Where $M_{ng\,m}{}^{-3}$ is the metal as mass per volume, M_{ppm} is the metal concentration in 10 mL from digestion and V_{std} is the standard volume of air sampled. (One ppm in a 10 mL sample = 10 ng).

Table 15: Results of weighing of cellulose nitrate filters, showing average deviation from the mean. All results in μg.

	WEIGH 1	WEIGH 2	WEIGH 3	WEIGH 4	WEIGH 5	MEAN WEIGHT	AVE. DEV FROM MEAN
DATE	02/12/97	04/12/97	07/12/97	05/01/98	07/01/98		
TEMP	19	19	22	19	20		
RH	38	28	38	34	32		
FILTER NO							
WTES\0.20\001			99953	99733	99605	99764	126
WTES\0.20\002			100379	106180	106081	104213	2556
WTES\0.20\003			102128	101951	101842	101974	103
WTES\0.20\004			101312	101101	101021	101145	112
WTES\0.20\005			100533	100322	100276	100377	104
WTES\0.45\001			89367	89209	89115	89230	91
WTES\0.45\002			88870	88596	88548	88671	132
WTES\0.45\003			90411	90251	90157	90273	92
WTES\0.45\004			89773	89319	89219	89437	224
WTES\0.45\005			89814	89631	89578	89674	93
WTES\0.45\005			89876	89681	89657	89738	92
WTES\0.65\001		79486	74503	78838	78771	77900	1698
WTES\0.65\002		79734	76216	79397	79246	78648	1216
WTES\0.65\003		80184	77207	77024	76931	77837	1174
WTES\0.65\004		77858	79522	79321	79248	78987	565
WTES\0.65\005		76514	76220	76051	75967	76188	179
WTES\0.65\006		73394	74503	74349	74276	74131	368
mtes\mce\37\0.8\1	47901	47661	47679	47602	47559	47680	88
mtes\mce\37\0.8\1	48337	48105	48111	48041	47996	48118	88
mtes\mce\47\0.45\1	78467	79135	77579	77395	77331	77981	656
mtes\mce\47\0.45\2	78559	77999	77519	77402	77305	77757	418
mtes\mce\47\0.45\3	80207	78455	77554	77452	77421	78218	891
mtes\mce\47\0.65\1	78552	78435	77976	77875	77819	78131	290
mtes\mce\47\0.65\2	79612	79726	79137	79012	77991	79096	475
mtes\mce\47\0.8\1	81271	81266	81601	80582	80537	81051	394
mtes\mce\47\0.8\2	81956	82031	81651	81468	81433	81708	229

Table 16: Results of in weighing of Gelmans PTFE filters showing the level of accuracy achieved. All results are in μg.

FILTER NO	WEIGHT 1 RH=34 TEMP=19	WEIGHT 2 RH=32 TEMP=20	IN WEIGHT (AVE)	DIFF.
gtes\PTFE\2.0\01	125987	125982	125985	5
gtes\PTFE\2.0\02	128488	128491	128490	-3
gtes\PTFE\2.0\03	129702	129705	129704	-3
gtes\PTFE\2.0\04	128734	128723	128729	11
gtes\PTFE\2.0\05	120777	120776	120777	1
gtes\PTFE\2.0\06	133733	133727	133730	6
gtes\PTFE\2.0\07	126443	126435	126439	8
gtes\PTFE\2.0\08	125547	125541	125544	6
gtes\PTFE\2.0\09	135661	135653	135657	8
gtes\ZEF\1.0\01	267626	267622	267624	4
gtes\ZEF\1.0\02	261805	261802	261804	3
gtes\ZEF\1.0\03	269783	269782	269783	1
gtes\ZEF\0.5\01	277590	277591	277591	-1
gtes\ZEF\0.5\02	280996	280997	280997	-1
gtes\ZEF\0.5\03	283049	283049	283049	0

Table 17: Results of out weighing of Gelmans PTFE filters showing the level of accuracy achieved. All results are in μg.

FILTER NO	WEIGHT 1 RH=34 TEMP=19	WEIGHT 2 RH=32 TEMP=20	OFF WEIGHT (AVE)	DIFF.
gtes\PTFE\2.0\01	126052	126051	126052	1
gtes\PTFE\2.0\02	128766	128766	128766	0
gtes\PTFE\2.0\03	130621	130619	130620	2
gtes\PTFE\2.0\04	129568	129569	129569	-1
gtes\PTFE\2.0\05	120895	120831	120863	64
gtes\PTFE\2.0\06	133801	133802	133802	-1
gtes\PTFE\2.0\07	126462	SAMPLE	LOST	****
gtes\PTFE\2.0\08	****	****	****	(BLANK)
gtes\PTFE\2.0\09	****	****	****	(BLANK)
gtes\ZEF\1.0\01	267728	267721	267725	7
gtes\ZEF\1.0\02	262048	26046	262048	-2
gtes\ZEF\1.0\03	269825	269828	269825	3
gtes\ZEF\0.5\01	277791	277790	277791	1
gtes\ZEF\0.5\02	281072	281068	281070	4
gtes\ZEF\0.5\03	283163	283162	283163	1

Table 18: Summary of filter exposure results.

FRACTION	FILTER NUMBER	TIME PERIOD (hours)	PARTICULATE MASS µg	STANDARD VOLUME m^3	MASS $\mu g\ m^{-3}$
PM_{10}	gtes/PTFE/2.0/01	8:00	67	2.392	28
	gtes/PTFE/2.0/02	24:00	276.5	7.289	38
	gtes/PTFE/2.0/06	4:00	71.5	4.235	17
	gtes/PTFE/2.0/07	8:00	23.0	TEAR IN FILTER	---
$PM_{2.5}$	gtes/PTFE/2.0/03	24:00	916.5	25.472	36
	gtes/PTFE/2.0/04	24:00	840.0	25.454	33
	gtes/PTFE/2.0/05	4:00	86.5	4.142	21
	gtes/ZEF/ 1.0/01	4:00	100.5	4.391	23
	gtes/ZEF/ 1.0/02	4:00	NO RESULT	---	---
	gtes/ZEF/ 0.5/03	4:00	113.5	3.257	35
PM_1	gtes/ZEF/ 1.0/03	4:00	NO RESULT	---	---
	gtes/ZEF/0.5/01	4:00	200.0	4.166	48
	gtes/ZEF/ 0.5/02	4:00	73.5	4.352	17

Table 19: Results of ICP analysis using 1000ppm standards.

STANDARD = 1000 ppm	UNIT	Cr	Zn	Cd	Pb	Ni	Cu
GTES/PTFE/2.0/01	Ppm	5	-94	10	46	320	45
STD VOL = 2.39 m^3	CV	200	34	53	45	25	8
FRACTION=PM_{10}	ng m^{-3}	21	-393	42	192	1339	188
GTES/PTFE/2.0/03	Ppm	8	276	16	251	322	131
STD VOL = 25.47 m^3	CV	72	8	19	20	1	1
FRACTION=$PM_{2.5}$	ng m^{-3}	3	108	6	99	127	51
GTES/PTFE/2.0/04	Ppm	5	177	6	273	287	56
STD VOL = 25.45 m^3	CV	78	3	23	6	6	7
FRACTION=$PM_{2.5}$	ng m^{-3}	2	70	2	109	114	22
GTES/PTFE/2.0/05	Ppm	5	733	10	28	276	56
STD VOL = 4.14 m^3	CV	157	10	16	104	7	14
FRACTION=$PM_{2.5}$	ng m^{-3}	12	1770	24	68	667	135
GTES/PTFE/2.0/06	Ppm	7	-224	2	26	249	-19
STD VOL = 4.25 m^3	CV	85	8	126	61	2	2
FRACTION=PM_{10}	ng m^{-3}	16	-527	5	61	586	-45
AVE PM10	ng m^{-3}	19	-460	24	127	963	72
AVE PM2.5	ng m^{-3}	6	974	11	92	303	69
% PM2.5 TO PM10		32	-212	46	72	31	96

CV=coefficient of variation (variation in replicate analysis).

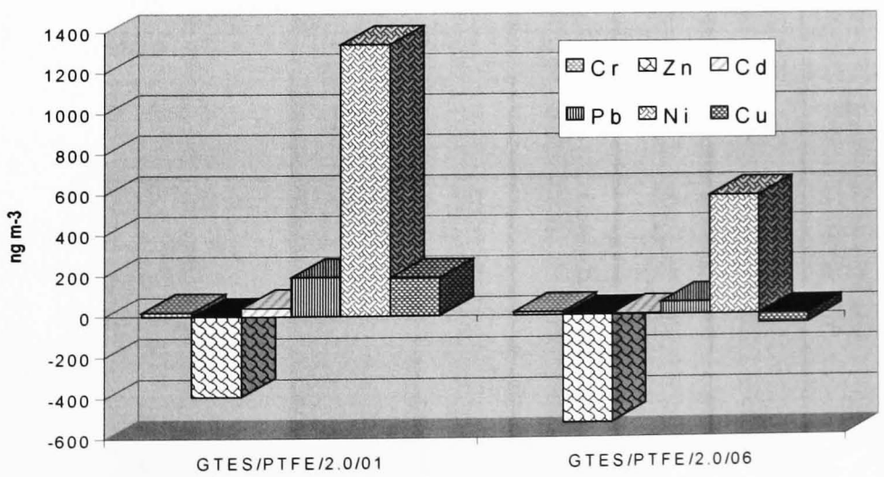
Table 20: Results of ICP analysis using 250ppm standards.

STANDARD = 250 ppm	UNIT	Cr	Zn	Cd	Pb	Ni	Cu
GTES/PTFE/2.0/01	**Ppm**	19	285	15	28	162	103
STD VOL = 2.39 m^3	**CV**	2.2	7.8	49.9	92.9	8.5	6.1
FRACTION=**PM_{10}**	**ng m^{-3}**	80	1193	71	117	678	431
GTES/PTFE/2.0/03	**Ppm**	26	645	18	218	345	193
STD VOL = 25.47 m^3	**CV**	15.4	4.2	1.1	5.3	0.3	5.4
FRACTION=**$PM_{2.5}$**	**ng m^{-3}**	10	253	7	86	136	76
GTES/PTFE/2.0/04	**Ppm**	19	444	9	222	170	97
STD VOL = 25.45 m^3	**CV**	4.2	4.3	0	8.3	7.9	1.3
FRACTION=**$PM_{2.5}$**	**ng m^{-3}**	8	174	4	87	67	38
GTES/PTFE/2.0/05	**Ppm**	23	815	13	45	146	94
STD VOL = 4.14 m^3	**CV**	16.1	2.4	22	5.1	7.6	0.4
FRACTION=**$PM_{2.5}$**	**ng m^{-3}**	56	1969	31	109	353	227
GTES/PTFE/2.0/06	**Ppm**	17	200	7	95	125	37
STD VOL = 4.25 m^3	**CV**	47.1	5.5	2.8	10.9	8.6	15.4
FRACTION=**PM_{10}**	**ng m^{-3}**	40	471	16.5	224	294	87
AVE PM10	**ng m^{-3}**	60	832	38	171	486	259
AVE PM2.5	**ng m^{-3}**	25	799	14	93	185	114
% PM2.5 TO PM10		42	96	37	54	38	44

CV=coefficient of variation (variation in replicate analysis).

Figure 35: Metal concentrations obtained with 1000 ppm standards using ICP analysis; a) for PM10 b) for PM2.5.

a)



b)

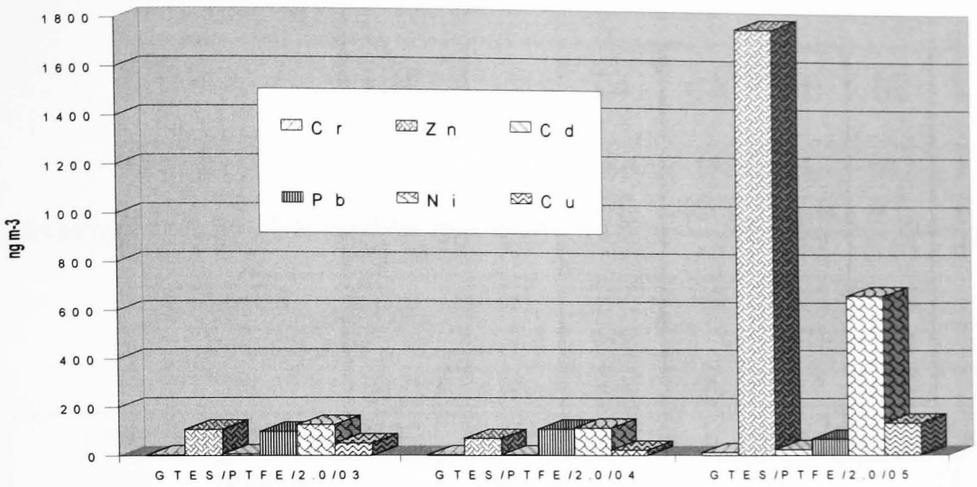
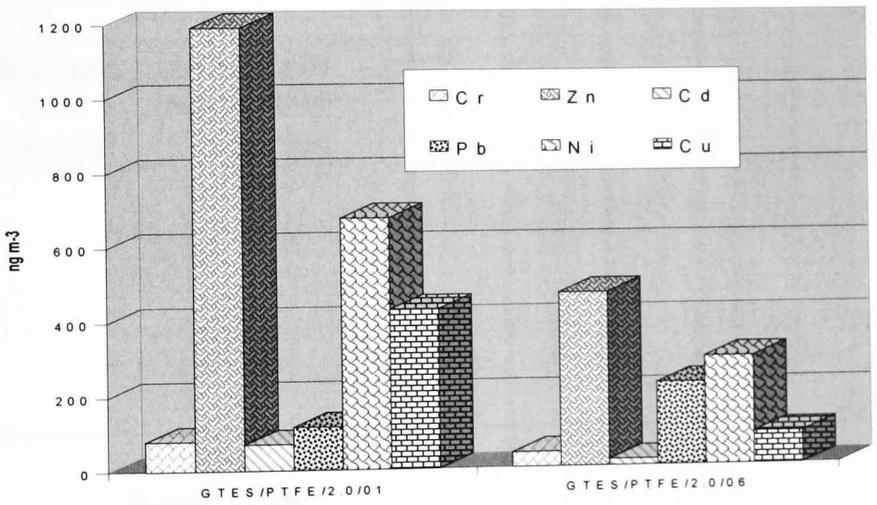


Figure 36: Showing metal concentrations obtained with 250ppm standards using ICP analysis; a) for PM_{10} b) for $PM_{2.5}$.

a)



b)

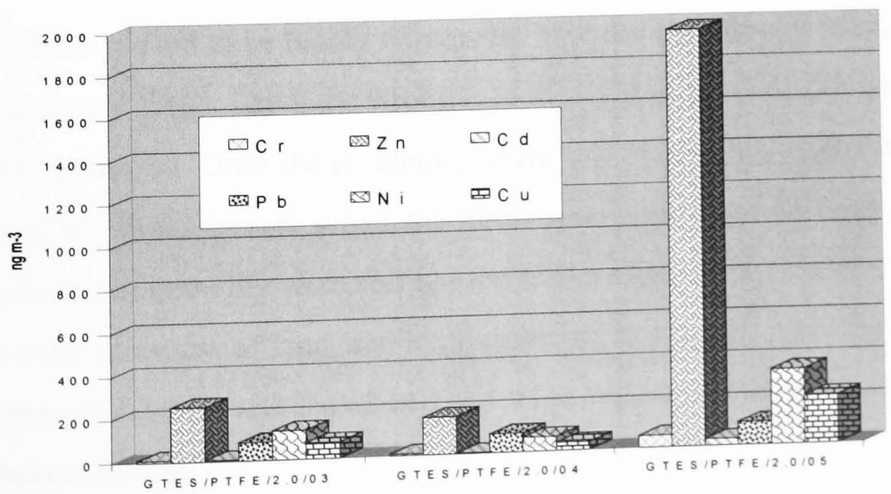


Table 21: Average results obtained in this study and those reported by Williams *et al* (1996).

		AVERAGE RESULT ng m^{-3}					
1000 PPM STANDARD	CUT POINT	Cd	Cr	Cu	Ni	Pb	Zn
	PM10	24	17	93	864	107	283
	PM2.5	4	3	37	117	103	89
		AVERAGE RESULT ng m^{-3}					
250 PPM STANDARD	CUT POINT	Cd	Cr	Cu	Ni	Pb	Zn
	PM10	37	58	248	442	150	1211
	PM2.5	5	9	57	101	86	214
		REPORTED VALUE ng m^{-3}					
Williams *et al* (1995)	AVE (TSP)	***	19	5	23	755	745
	MRH (TSP)	***	15	12	32	884	1599
	ERH (TSP)	***	19	14	78	916	1965

DISCUSSION

Filter Type

The cellulose filters proved to be highly susceptible to static and changes in relative humidity. The author discovered that wearing the wrong type of clothing could render weighing useless due to the static generated. Once the problem of static was resolved (two alpha sources were used to create an ion cloud through which the filters were passed and an earth strap was worn), the problems of humidity were still apparent. The ranges in individual filter weights were in some cases in excess of 1mg, and in all cases, so far beyond the range of accuracy required that the entire batch was abandoned and more expensive but non-hydrophilic PTFE filters were chosen for use.

The PTFE filter proved to be straight forward to weigh (Table 2), only the two measurements were required to achieve accuracy averaging a range of 4 μg for the initial weighing and 2 μg for the off weighing (ignoring the results for gtes\PTFE\2.0\05 which was anomalous). These filters were found to be reliable and suitable for the restrictions imposed by the clean room facilities at Middlesex University. The type with integral PNP support were heavier but with a counter weight proved reliable to weigh, they were not very susceptible to static and filter masses remained stable between 28 & 21% relative humidity (19°C).

In comparison, cellulose nitrate filters showed average accuracy ranges of 641 μg, a minimum change of 181 μg and a maximum change of 1804 μg.

Mass Concentrations

The results of weighing of the clean PTFE filters (in weighing) can be seen in Table 2, and of the weighing of the same filters after exposure (out weighing) are summarised in Table 3.

The exposure and particulate mass per unit volume collected are summarised in Table 9 Appendix B:1.

It can be seen from Tables 2 and 3 that only two weighings were necessary in each case to achieve the levels of accuracy stipulated by the weighing protocol, with the two following exceptions. On one occasion the difference was 11μg (gtes\PTFE\2.0\04, Table 2). The reasons for this were not determined. However, it is clear that the result is anomalous.

Filter no. gtes\PTFE\2.0\05 showed a loss of 64 μg between out weghings (Table 3), this again was anomalous and isolated, this may have been due to particulate associated moisture or VOCs (i.e. a rain drop or oil from the sample head). This sample was ignored in the rest of the study.

The results in Table 4 show PM_{10} concentrations ranging from 17 μg m^{-3} to 38 μg m^{-3} with an average of 28 μg m^{-3}). These concentrations are well within the expected range 20-30 μg m^{-3}

rising to around 50 μg m^{-3} in ambient air (QUARG 1996). The results for $PM_{2.5}$ range from 21 μg m^{-3} to 36 μg m^{-3} always showing lower concentrations than those of PM_{10} for the same period (except for the 15/01/98 where the $PM_{2.5}$ filter continued to lose weight for a prolonged period, the reasons for this were not resolved).

A great deal was learned from the study both about particulate air pollution and the operation of the Partisol and AirMetric. As can be seen in Table 3, problems occurred with the Partisol around the 23/01/98, this appeared to be the result of a software corruption, possibly caused by a power outage or surge (ETI technical support staff *Pers. Comm.* 1998). The EPROM was wiped and recallibrated on the 26/01/98 and the problems appeared to be solved. However on the 28 & 29/01/98 a leak in the hub unit became apparent, as this filter was heavily soiled in comparison to that of satellite 1 (simultaneous sample) it would seem that the leak was above the filter housing and the separator. On leak testing the leak proved to be in the sample head itself and was remedied by applying a small quantity of silicone grease on the affected area.

ICP Analysis

Tables 5 and 6 shows the results of ICP analysis of the digested samples. The first run was performed using 1000ppm standards (Table 5) but the metals were being detected at levels as low as 2.0 ppm which is close to the limit of detection and towards the limits of the tolerance of the calibration curve, generated by the blank and standard, resulting in the poor coefficients of variance throughout. The results can be seen to be unreliable (demonstrated by the high coefficients of variance) moving into negative concentrations in two cases: Zn and Cu both show negative concentrations (see graphs 1: a) and b)). This is due to the innapropriate standards used resulting in a 'reflection'. It is worth noting that despite the inaccuracy of the data, PM_{10} concentrations were greater than those of $PM_{2.5}$ as would be expected.

The standards were modified to 250 ppm and analysis was repeated the results (Table 6), all showed positive concentrations and good correlation between calculated mass/volume concentrations. From this table it can be seen that the CV's are generally better than 10% (4% being the generally accepted limit of precision for the replicates) and so more confidence can

be held in the results. One factor affecting the accuracy here was the fact that the ICP was not allowed to warm up for long enough reducing accuracy, it can be seen that the CV's improved after the first run. The $PM_{2.5}$ fraction shows a 37 to 54% contribution to the metal content of PM_{10} , the exception Zn (96%) may suggest contamination (or a different speciation that is present only in the a fine fraction). The results for Zn (GTES/PTFE/2.0/05) are notably higher and probably account for the high $PM_{2.5}$ contribution, highlighting the need for a large number of samples.

The standards used in this study were wholly inappropriate, as ICP analysis is dependent on the matrix it would be appropriate to use standards that reflect the ratios of the analytes in the sample matrix. This ensures that the individual analytes are subjected to a more representative set of interferences. A suitable standard matrix in this case would consist of Cr -75 ppb, Zn - 1000 ppb, Cd - 50 ppb, Pb - 200 ppb, Ni - 500 ppb and Cu - 250 ppb.

The metal concentrations obtained were higher for the PM_{10} fraction than would be expected (table 7). As the cut off point of the sampler is dependent on the aerodynamic diameter of the particle in question, metals may be present as salts which are hydrophilic and so will tend to absorb water and increase in aerodynamic diameter with increasing humidity decreasing the quantities found in the finer fraction.

Considering the results obtained using the 1000 ppm standards (graph 1 a) and b)) the mass/volume concentrations are unreliable, and so will be disregarded. Results obtained using 250 ppm standards (table 6, graph 2 a) and b)) show high values for Cr, Cu and Ni when compared with those obtained by Williams *et al* (199) for TSP (Table 7). This may be due in part to the samples being run for short periods (4 hr runs) over peak periods, therefore highlighting maximum concentrations which tend to occur during peak traffic periods. The small number of samples over a short time period could result in a period of high concentrations being highlighted, the larger number of samples over a longer time period in the main study will eliminate this problem.

Pb shows low values when compared with those obtained by Williams *et al* (1995) for TSP (table 7). This may be due in part to the elevated sampling position (≈10-15m), the distance from the road (≈30-40m) and possibly reflect the ratio of leaded fuel to unleaded fuel being

used by vehicles. Again the small number of samples acquired over a short time period mean that this could be a non-typical data set, this being eliminated in the final study.

Zn shows more typical values if not a little high, but considering the peak traffic samples this is a typical value (Williams *et al* 1995).

CONCLUSIONS

- Cellulose Nitrate filters are useless unless static, temperature and humidity can be controlled tightly whilst conditioning and weighing.
- PTFE filters are more stable in varying humidity conditions, are not as susceptible to static and are suitable for metals analysis, therefore these are recommended for this study.
- The PTFE filters with PNP support ring are easy to handle but are more expensive than those with integral PNP support. The latter also offer pore sizes of 1.0 μm and 0.5 μm as opposed to 2.0 μm for the former, Therefore the author recommends the latter: Gelmans; 0.5 μm pore, ZEFLOUR filters.
- The samplers were found to be simple to operate however the Partisol proved to be problematic at times. This will not be a problem in the main study as the suppliers offer a good level of support and many basic pitfalls are determined here.
- The digestions can be made up to 10 ml, this allows for 3 or more replicates during analysis of six metals.
- However, due to the time scales involved and the requirement to prioritise the number of samples collected in the main study, metals analysis will be dropped for the main study.

Appendix Bb

(RAW RESULTS FROM PILOT STUDY)

Table 8: Results of weighing clean cellulose nitrate filters supplied by two separate manufacturers. Expressed as μg, (RH/T = relative humidity/ temperature.)

FILTER NO	RH\TE	DATE	WEIGHT	RH/T	DATE	WEIGHT	RH/T	DATE	WEIGHT	RH/T	DATE	WEIGHT	RH/T	DATE	WEIGHT
WTES\0.20\001							38/22	07/12/97	99.953	34/19	05/01/98	99.733	32/20	07/01/98	99.605
WTES\0.20\002							38/22	07/12/97	100.379	34/19	05/01/98	106.18	32/20	07/01/98	106.081
WTES\0.20\003							38/22	07/12/97	102.128	34/19	05/01/98	101.951	32/20	07/01/98	101.842
WTES\0.20\004							38/22	07/12/97	101.312	34/19	05/01/98	101.101	32/20	07/01/98	101.021
WTES\0.20\005							38/22	07/12/97	100.533	34/19	05/01/98	100.322	32/20	07/01/98	100.276
WTES\0.45\001							38/22	07/12/97	89.367	34/19	05/01/98	89.209	32/20	07/01/98	89.115
WTES\0.45\002							38/22	07/12/97	88.87	34/19	05/01/98	88.596	32/20	07/01/98	88.548
WTES\0.45\003							38/22	07/12/97	90.411	34/19	05/01/98	90.251	32/20	07/01/98	90.157
WTES\0.45\004							38/22	07/12/97	89.773	34/19	05/01/98	89.319	32/20	07/01/98	89.219
WTES\0.45\005							38/22	07/12/97	89.814	34/19	05/01/98	89.631	32/20	07/01/98	89.578
WTES\0.45\005							38/22	07/12/97	89.876	34/19	05/01/98	89.681	32/20	07/01/98	89.657
WTES\0.65\001				28/19	04/12/97	79.486	38/22	07/12/97	74.503	34/19	05/01/98	78.838	32/20	07/01/98	78.771
WTES\0.65\002				28/19	04/12/97	79.734	38/22	07/12/97	76.216	34/19	05/01/98	79.397	32/20	07/01/98	79.246
WTES\0.65\003				28/19	04/12/97	80.184	38/22	07/12/97	77.207	34/19	05/01/98	77.024	32/20	07/01/98	76.931
WTES\0.65\004				28/19	04/12/97	77.858	38/22	07/12/97	79.522	34/19	05/01/98	79.321	32/20	07/01/98	79.248
WTES\0.65\005				28/19	04/12/97	76.514	38/22	07/12/97	76.22	34/19	05/01/98	76.051	32/20	07/01/98	75.967
WTES\0.65\006				28/19	04/12/97	73.394	38/22	07/12/97	74.503	34/19	05/01/98	74.349	32/20	07/01/98	74.276
mtes\mce\37\0.8\1	38/19	02/12/97	47.901	28/19	04/12/97	47.661	38/22	07/12/97	47.679	34/19	05/01/98	47.602	32/20	07/01/98	47.559
mtes\mce\37\0.8\1	38/19	02/12/97	48.337	28/19	04/12/97	48.105	38/22	07/12/97	48.111	34/19	05/01/98	48.041	32/20	07/01/98	47.996
mtes\mce\47\0.45\1	38/19	02/12/97	78.467	28/19	04/12/97	79.135	38/22	07/12/97	77.579	34/19	05/01/98	77.395	32/20	07/01/98	77.331
mtes\mce\47\0.45\2	38/19	02/12/97	78.559	28/19	04/12/97	77.999	38/22	07/12/97	77.519	34/19	05/01/98	77.402	32/20	07/01/98	77.305
mtes\mce\47\0.45\3	38/19	02/12/97	80.207	28/19	04/12/97	78.455	38/22	07/12/97	77.554	34/19	05/01/98	77.452	32/20	07/01/98	77.421
mtes\mce\47\0.65\1	38/19	02/12/97	78.552	28/19	04/12/97	78.435	38/22	07/12/97	77.976	34/19	05/01/98	77.875	32/20	07/01/98	77.819
mtes\mce\47\0.65\2	38/19	02/12/97	79.612	28/19	04/12/97	79.726	38/22	07/12/97	79.137	34/19	05/01/98	79.012	32/20	07/01/98	77.991
mtes\mce\47\0.8\1	38/19	02/12/97	81.271	28/19	04/12/97	81.266	38/22	07/12/97	81.601	34/19	05/01/98	80.582	32/20	07/01/98	80.537
mtes\mce\47\0.8\2	38/19	02/12/97	81.956	28/19	04/12/97	82.031	38/22	07/12/97	81.651	34/19	05/01/98	81.468	32/20	07/01/98	81.433

Table 9: Results of weighing a) clean and b) loaded Gelmans PTFE filters.

a)

FILTER NO	RH/TE	DATE		RH/TE	DATE		IN WEIGHT
gtes\PTFE\2.0\01	34/19	05/01/98	125.987	32/20	07/01/98	125.982	**125.985**
gtes\PTFE\2.0\02	34/19	05/01/98	128.488	32/20	07/01/98	128.491	**128.490**
gtes\PTFE\2.0\03	34/19	05/01/98	129.702	32/20	07/01/98	129.705	**129.704**
gtes\PTFE\2.0\04	34/19	05/01/98	128.734	32/20	07/01/98	128.723	**128.729**
gtes\PTFE\2.0\05	34/19	05/01/98	120.777	32/20	07/01/98	120.776	**120.777**
gtes\PTFE\2.0\06	34/19	05/01/98	133.733	32/20	07/01/98	133.727	**133.730**
gtes\PTFE\2.0\07	34/19	05/01/98	126.443	32/20	07/01/98	126.435	**126.439**
gtes\PTFE\2.0\08	34/19	05/01/98	125.547	32/20	07/01/98	125.541	**125.544**
gtes\PTFE\2.0\09	34/19	05/01/98	135.661	32/20	07/01/98	135.653	**135.657**
gtes\ZEF\1.0\01	23/19	21/01/98	267.626	27/19	23/01/98	267.622	**267.624**
gtes\ZEF\1.0\02	23/19	21/01/98	261.805	27/19	23/01/98	261.802	**261.804**
gtes\ZEF\1.0\03	23/19	21/01/98	269.783	27/19	23/01/98	269.782	**269.783**
gtes\ZEF\0.5\01	23/19	21/01/98	277.590	27/19	23/01/98	277.591	**277.591**
gtes\ZEF\0.5\02	23/19	21/01/98	280.996	27/19	23/01/98	280.997	**280.997**
gtes\ZEF\0.5\03	23/19	21/01/98	283.049	27/19	23/01/98	283.049	**283.049**

b)

FILTER NO	RH/TE	DATE	WEIGH	RH/TE	DATE	WEIGH	OUT
gtes\PTFE\2.0\01	22/19	23/01/98	126.052	21/19	26/01/98	126.051	**126.052**
gtes\PTFE\2.0\02	24/19	19/01/98	128.766	23/19	21/01/98	128.766	**128.766**
gtes\PTFE\2.0\03	24/19	19/01/98	130.621	23/19	21/01/98	130.619	**130.620**
gtes\PTFE\2.0\04	24/19	19/01/98	129.568	23/19	21/01/98	129.569	**129.569**
gtes\PTFE\2.0\05	24/19	19/01/98	120.895	23/19	21/01/98	120.831	**120.863**
gtes\PTFE\2.0\06	24/19	19/01/98	133.801	23/19	21/01/98	133.802	**133.802**
gtes\PTFE\2.0\07	24/19	19/01/98	126.462	23/19	21/01/98	TORE	**126.462**
gtes\PTFE\2.0\08	24/19	19/01/98	****	23/19	21/01/98	CONTR	****
gtes\PTFE\2.0\09	24/19	19/01/98	****	23/19	21/01/98	CONTR	****
gtes\ZEF\1.0\01	21/19	28/01/98	267.728	28/19	29/01/98	267.721	**267.7245**
gtes\ZEF\1.0\02	28/19	29/01/98	262.048				**262.048**
gtes\ZEF\1.0\03	28/19	29/01/98	269.825				**269.825**
gtes\ZEF\0.5\01	20/19	27/01/98	277.791	21/19	28/01/98	277.79	**277.7905**
gtes\ZEF\0.5\02	21/19	28/01/98	281.072	28/19	29/01/98	281.068	**281.07**
gtes\ZEF\0.5\03	20/19	27/01/98	283.163	21/19	28/01/98	283.162	**283.1625**

UNITS:- RH=% TEMP=^{O}C WEIGHTS= mg.

Table 10: Exposure information for PTFE filters with final PM mass. Raw results and calculated particulate masses from the pilot study.

FILTER NUMBER	STATION ID.	CUT POINT µm	SAMPLE DATE	TIME PERIOD hours	PERIOD TYPE❁	CLEAN WEIGHT mg	LOADED WEIGHT mg	PM MASS mg	VOL_{ST} M^3	MASS $\mu g\ m^{-3}$	COMMENTS
gtes\PTFE\2.0\	AI1	10	21/01/98	8.00	MR+E	125.985	126.051	67.0	2.392	28	
gtes\PTFE\2.0\	AI1	10	10/01/98	24.00	D,WE	128.490	128.766	276.5	7.289	38	
gtes\PTFE\2.0\	PH	2.5	10-	24.00	D,WE	129.704	130.62	916.5	25.47	36	
gtes\PTFE\2.0\	P1	2.5	10-	24.00	D,WE	128.729	129.568	840.0	25.45	33	
gtes\PTFE\2.0\	P1	2.5	15/01/98	4.00	ER	120.777	120.863	86.5	4.142	21	FALLING (64ug)
gtes\PTFE\2.0\	PH	10	15/01/98	4.00	ER	133.730	133.801	71.5	4.235	17	
gtes\PTFE\2.0\	AI1	10	15-	8.00	ER+M	126.439	126.462	23.0	TOR	***	TORE IN
gtes\PTFE\2.0\	***	***	***	***	***	125.544	***	CONTROL	***	***	**135.649**
gtes\PTFE\2.0\	***	***	***	***	***	135.657	***	CONTROL	***	***	**125.542**
gtes\ZEF\1.0\0	P1	2.5	26/01/98	4.00	MR+E	267.624	267.724	100.500	4.391	23	
gtes\ZEF\1.0\0	P1	2.5	28-	4.00	MR+E	261.804	**	**	**	**	
gtes\ZEF\1.0\0	PH	1	28-	4.00	MR+E	269.783	**	**	**	**	
gtes\ZEF\0.5\0	PH	1	23/01/98	4.00	ER	277.591	277.790	200.000	4.166	48	
gtes\ZEF\0.5\0	PH	1	26/01/98	4.00	MR+E	280.997	281.07	73.500	4.352	17	
gtes\ZEF\0.5\0	P1	2.5	23/01/98	4.00	ER	283.049	283.162	113.500	3.257	35	

❁ D = (all) Day, MR = Morning Rush (hour), ER = Evening Rush (hour), WE = Week End.

A Winter Study for Characterisation of Particulate Air Pollution at a Site on the Archway Road (A1) London with Comparisons to a Previous Summer Study at the Same Site.

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Towards the requirements for the completion of the qualification:
BSc in Environmental Science and Technology.

MAY 1999

Work undertaken at Middlesex University, Bounds Green, Bounds Green Road, LONDON, N11 2NQ

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1. ABSTRACT

Collocated, winter, 24 hour samples were taken for TSP (using a Rotheroe and Mitchell L30 sampler), PM_{10}, $PM_{2.5}$ and PM_1 (using a Partisol sampler), rush hour samples were taken for TSP (AM and PM) and for PM_{10} (combined, using a portable Airmetric Minivol) at a site on Archway Road, A1, London from March 01 1999 to March 28 1999. A second, Airmetric PM_{10} monitor was compared to the Partisol (a USAEPA standard method) on the basis of 24 hour samples. On the basis of regression analysis this was found to be a robust PM_{10} monitor with a tendency to oversample, reporting 112% of Partisol results. Partisol PM_{10} and $PM_{2.5}$ results were compared to AUN network sites and were found to be comparable to inner city London roadside sites but showed several higher peak values. Significant site-specific correlations were found for all particulate fractions during this study (based on 24 hour samples) indicating one dominant source. This source was concluded to be traffic on the basis of rush hour PM_{10} concentrations. Rush hours were found to contribute around 50% of daily PM_{10}. $PM_{2.5}$ was found to contribute 79% of PM_{10}, whilst PM_1 was found to contribute 68% and 85% to PM_{10} and $PM_{2.5}$ respectively. These were found to be slightly elevated in comparison to contributions of 76%, 62% and 81% respectively, found in a previous study at the same site in summer 1998. Analysis of weekday and weekend summary statistics revealed that winter weekday concentrations for all fractions were slightly elevated over winter weekend concentrations, this was especially notable in rush hour data and particular for TSP AM rush hour data, this was consigned to the effects of cold starts and traffic patterns. These patterns were not evident in the summer data. The effects of resuspension on TSP were notably absent from the winter study in comparison to winter data.

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and finally,

to Grace for her knowledge of grammar

oh, and the tea and biscuits!! ;-)

3. AIMS

- To obtain collocated winter samples at a site on Archway Road, A1, London for:
  - ⊗ 24 hour PM_{10}, $PM_{2.5}$, PM_1 and TSP
  - ⊗ Rush hour samples for TSP (AM and PM) and PM_{10} (combined)
- To collocate an Airmetric Minivol PM_{10} sampler and validate it on the basis of 24 hour samples.
- To compare 24 hour PM_{10} and $PM_{2.5}$ concentrations with AUN site data.
- To investigate the contributions of the finer fractions to PM_{10} at the site.
- To investigate the impact of the rush hours on 24 hour PM_{10} and TSP concentrations and therefore the relevance of traffic as a source in this area.
- To compare site relationships between all fractions using regression analysis.
- To analyse all data on the basis of the whole data set, week days and week ends.
- To compare all the above findings with previous data obtained in an identical summer study undertaken at the site in 1998.

4. A GENERAL INTRODUCTION TO PARTICULATE AIR POLLUTION

4.1 What is Particulate Air Pollution?

Particulate air pollution refers to a complex mixture of chemicals that are suspended in the atmosphere. One common term used to describe this mixture is aerosol. This is defined in the third report of QUARG (1996) as: "A suspension of solid or liquid particles in the atmosphere". Ambient aerosol is a term used to describe the typical aerosol of a given area at a given point in time. Strictly this not only includes the particulates, but also the surrounding air that contains them (Wilson R and Spengler J D, 1996).

It is important to understand that the nature of particulate pollution is defined by the system that is used to monitor it. This requires a basic understanding of some of the characteristics of this pollutant.

4.1.1 Aerodynamic Diameter

It is well established in the literature that particulates are described, primarily in terms of their aerodynamic diameter rather than their actual diameter. Aerodynamic diameter (AD) is defined as the diameter of a given particle were it spherical and having a density of 1.0 g cm^{-3} (that of water) (QUARG 1996 and Wilson R and Spengler J D, 1996).

It is convenient to adopt this term for three reasons:

1. Firstly; the methods of monitoring specific size ranges rely on the manipulation of the particles in the aerosol by giving them a known velocity, therefore their separation is based on their inertia. This would be impossible to describe for all of the constituents yet can be conveniently covered by reference to the definition of AD (above).

2. Secondly; the length of time a given particulate will remain air borne is a function of its

density and volume, again it is impossible to define to all possible cases, the use of the AD definition gives the ability to define the range of particles which will remain air borne under any given conditions. This provides the capacity to describe any ambient aerosol in terms of it's size distribution.

3. Thirdly; as the physical processes governing the capacity of particulates to penetrate into the human (or other) respiratory system are the same processes used to monitor and define the ambient aerosol, use of the AD definition allows for the data obtained to be directly assessed in terms of health effects.

4.1.2 Typical Size Distributions and Sources of Ambient Aerosols

The size distributions of aerosols are more complex than may be expected; the shape of the distribution depends strongly on the method of representation (Figure 1). It is evident that in terms of number of particles versus diameter the greatest number lie in the sub-micron range, with numbers falling rapidly towards the 1.0 μm diameter range. If this was all the information available it may appear that the larger particles are insignificant. However when plotting surface or mass against diameter it becomes evident that the particles up to a size range of around 100μm diameter are highly significant.

If the ambient urban aerosol was to be graphically represented in terms of mass (or volume) versus aerodynamic diameter (or particle diameter) a tri-modal model would tend to emerge (Figure 2). These three modes are related to the sources and processes that contribute to the ambient aerosol and are known as the Nucleation mode, the Accumulation mode and the coarse mode.

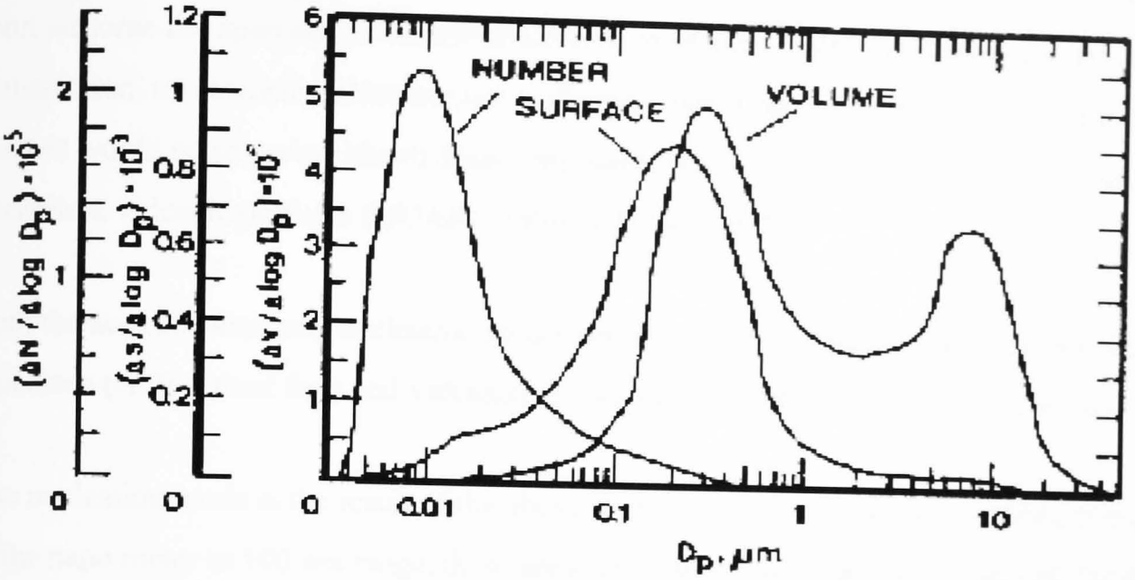


Figure 1: A distribution of particle number versus diameter, and the same simple aerosol plotted as surface and volume (or mass) versus diameter (source Colls J 1997).

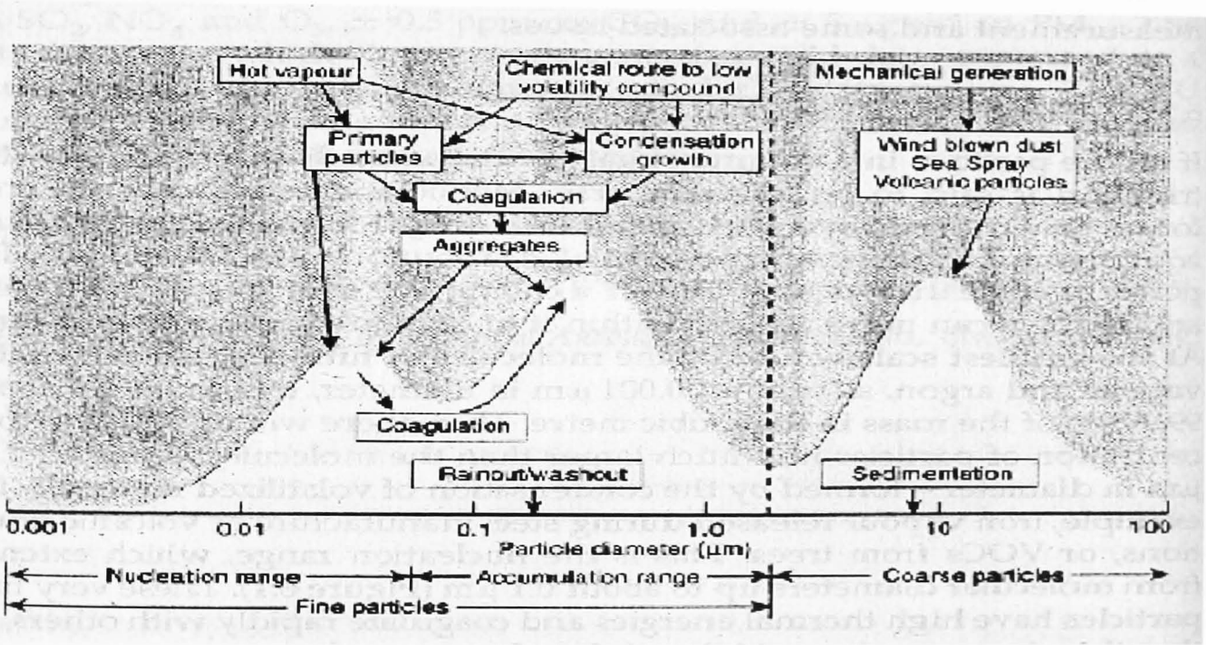


Figure 2: The idealised tri-modal size distribution; showing sources, sinks and the relationships between the modes (source Colls J 1997).

The coarse mode is a result of mechanical sources, dust from these sources tends to have a short airborne life span and so contributions tend to be local. Anthroprogenic sources being construction, mechanical industrial (saw mills etc.), tyre, brake wear and others. Natural sources would be any wind blown dusts (originally of mechanical origin), sea spray and the exception: volcanic particles (QUARG 1996 and Colls 1997).

Both the accumulation and nucleation modes are a result of combustion and hot industrial processes (with natural fires and vulcanism being the only substantial natural sources).

The nucleation mode is the result of the above high temperature processes emitting particles in the nano meter to 100 nm range, these are known as primary particulates and tend to be very short lived as they provide the nuclei for the processes which form the accumulation mode (QUARG 1996 and Colls 1997).

The accumulation mode results from the coagulation and aggregation of primary particles and from the condensative growth of the nuclei that provide a large surface area on which hot vapours can condense. Particles in this mode may grow up to the 1.0-3.0 μm size range but do not move into the coarse mode. Particles of this size tend to be removed through wash out/rain out (QUARG 1996 and Colls 1997).

4.2 Primary And Secondary Aerosols

Primary emissions can be of both anthroprogenic and natural origin. They refer to those particulates that remain airborne in the same state as the emission. The life span of primary particulates is dependent not only on the size and mass of the particle, but also on it's reactivity, that of the aerosol it is emitted into and the ambient conditions. The urban environment has a large enough number of anthroprogenic sources to cause a specific type of ambient aerosol which is a precursor to secondary particulate production under the right conditions (i.e. NO_x, O_3 and SO_2 from traffic).

Secondary emissions are the result of gas-to-particle conversion processes (Wilson R and Spengler J D, 1996). This refers to those processes which result in the formation of new particulates in the atmosphere as a consequence of the condensation of hot vapours, the reactions between gases and existing particulates, and the changes in speciation of interacting particulates (i.e. the conversion of SO^{2-} to H_2SO_4 by oxidation). These can result in photochemical smog pollution events when they are associated with ozone (O_3) events. One common conversion process is of SO_2 to particulate sulphates such as ammonium sulphate: $(NH_4)_2SO_4$; another is the formation of particulate nitrates from NOx to form ammonium nitrate: NH_4NH_3 (Chan Y C 1997).

4.3 MONITORING OF PARTICULATES IN THE UK

The first method for estimating particulate concentrations was the Black Smoke (BS) stain method which was instigated in the UK in the twenties (Organisation for Economic Co-operation and Development 1964). A BS/SO_2 monitor in Kew gardens showed a tenfold decrease between 1922/3 and 1970/1 (QUARG 1996). This trend has continued since but is not as pronounced and the results are no longer as valid due to changes in aerosol composition (this will be addressed in more detail later). Levels fell rapidly until the eighties when the decline slowed, this may be due to the influence of traffic related smoke, which are primarily generated by diesel vehicles (QUARG 1993b). It should be remembered when considering the BS data that sites were originally planned to monitor areas of high concentrations and that this may be reflected in the trend observed (QUARG 1996).

It was later recognised that the BS method reflected one aspect of the ambient aerosol and the TSP methodology was introduced as a way of determining the total atmospheric particulate loading. It was later recognised that health effects associated with particulate pollution were more attributable to the fraction of SPM/TSP that penetrates beyond the nasal cavity; the thoracic particle mass. This has since been thoroughly reviewed in the UK by the Committee on the Health Effects of Air Pollution (COMEAP 1995). PM_{10} sampling was instigated as the result of research into the most relevant fraction for ambient

monitoring. The USA instigated $PM_{2.5}$ monitoring as a measure of the fraction of SPM/TSP that penetrates to the lungs and deep lung (the respirable fraction).

At present in the UK, the debate is open as to the significance of $PM_{2.5/1}$ as a cut point for fine fraction monitoring. The cut point for the fine fraction (nucleation and accumulation modes) is somewhere in the 1 to $_{2.5}$ μm AD region and therefore this fraction represents anthroprogenic contributions to the ambient aerosol (in the absence of natural combustion sources). Large scale monitoring of this fraction could be of use to scientists as it could offer large-scale information on the fine fraction (Dr B. Gorbunov *pers. Comm.*).

The current situation in the UK is that the Expert Panel on Air Quality (EPAQS) guide line of 50 μg m^{-3} as a 24 hr (running) average has become legislation through the National Air Quality Strategy (NAQS 1997) with an objective of achieving the same standard at the 99^{th} percentile level in the year 2005.

5. FACTORS AFFECTING PARTICULATE CONCENTRATIONS

The ambient concentrations of particulates can vary widely as a result of several contributing factors. The most immediate factor to consider will be the local sources, any combustion or industrial processes will contribute to the anthroprogenic aspect. Re-suspended soil and dusts, natural combustion and sea salts are common natural sources.

In addition to the local inputs particulate concentrations will vary with season, time of day and weather conditions as a result of mixing, dilution and dispersion. Some meteorological conditions will contribute to the production of a secondary aerosol, others will affect the efficiency of combustion processes and cold weather will result in the increased use of fuels for heating etc, and will therefore be a precursor for elevated concentrations. In this section the individual factors will be considered and the source of motor vehicles will be considered as it is a major source in the case of this study.

5.1 The Influence Of Weather On Particulate Concentrations

Weather has a subtle effect on particulate concentrations, this being due to the inability to separate the effects of one aspect from another. Large weather systems can have significant effects on a countrywide basis, with time lags as small as a few hours or less. Large weather systems from Europe may carry continental particulates into the UK (King A *et al* 1997 and Steadman 1996), this will be discussed later in more detail.

5.1.1 Wind speed

The effects of wind on particulate concentrations must be considered together with other perameters but can loosely be considered in terms of winter effects and summer effects.

During the winter, the wind tends to have a dilution and dispersion effect, reducing the ambient concentrations through dilution of local emissions. This can be said as the winter rains and precipitations tend to result in the suppression of deposited particulate matter and inhibit re-suspension. Summer winds however can reverse the winter trends, re-suspension of street and road dusts, soils, construction dust and sea salt aerosols all contribute to PM_{10} levels and especially TSP in the absence of precipitation.

Figure 3 shows the diurnal variations for PM_{10} and $PM_{2.5}$ with windspeed during a study under taken at Hodge hill, Birmingham by Harrison *et al* in 1995 (reported in 1997)., the influence of wind on the coarse fraction (<10μm AD $>_{2.5}$ μm AD) is evident. As wind speed increases so does PM_{10}, $PM_{2.5}$ remains relatively stable, the separation between the two being due to re-suspended dusts. The data for 22/12/1995 (Figure 4) can be used for comparison, showing how closely related the two fractions can be under other circumstances.

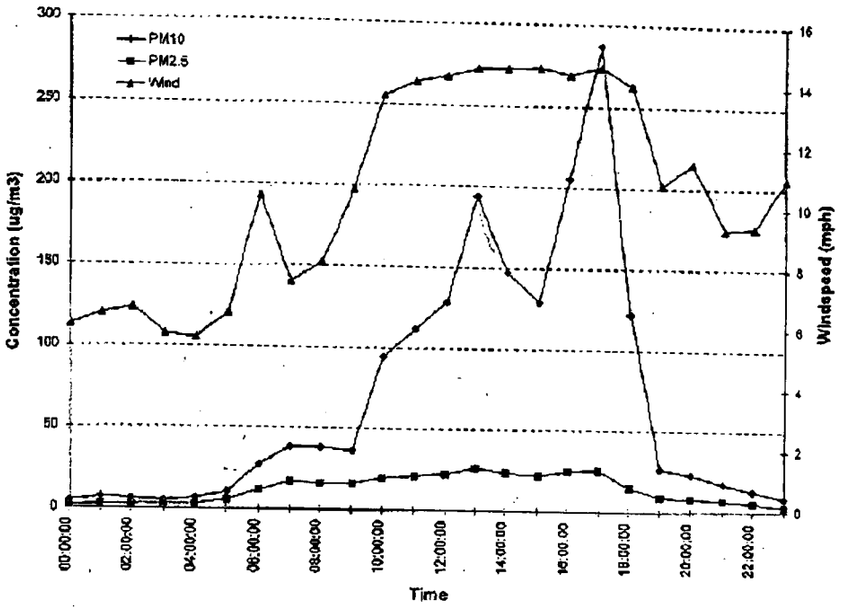


Figure 3: Diurnal variations in PM_{10}, $PM_{2.5}$ and local wind speed at Hodge hill, Birmingham 25/08/1995 (Harrrison *et al* 1997)

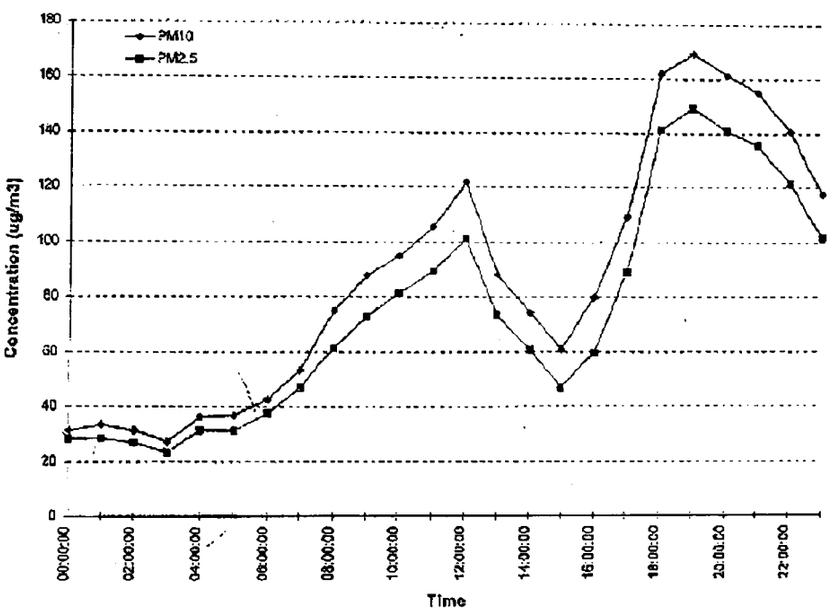


Figure 4: Diurnal variations in PM_{10} and $PM_{2.5}$ at Hodge Hill, Birmingham 22/12/1995 (Harrrison *et al* 1997)

5.1.2 Temperature

Again the effects are best considered in terms of winter and summer events. During winter periods there tends to be an inverse relationship between temperature and particulate concentration. This is largely due to the increased use of fuels for heat and the effects of cold starts and reduced engine efficiencies. The summer time trend is reversed showing a dependant relationship, this is often due to the build up of traffic related sources coupled with increased secondary production as the day progresses.

5.1.3 Sunshine

Particulate concentrations generally correlate well with sunshine. This is partly due to the fact that the main sources of particulates are of anthroprogenical origin and the local sources are emitted during daylight hours when people are more active. There is also the effect of sunshine during the summer when elevated temps and light stimulate the production of secondary particulates (QUARG 1996).

5.2 Diurnal Variations

As a result of the resolution of AUN sites, which provide 15 minute averages, there are now literally hundreds of data sets showing the daily patterns of PM_{10} concentrations (Broughton *et al* 1997). These generally exhibit a diurnal trend in urban areas. The lowest values occur during the early morning at around 3-5 AM when human activity is at its lowest. The concentrations generally climb and reach a maximum at around 8-9 AM, as a direct result of the build up of traffic in the morning rush to work (see Figure 3 and Figure 4). Levels then either remain relatively stable or, more generally, ebb to a middle value through the morning and afternoon, depending on the monitor's location. A second, often less pronounced peak is evident generally at around 6 PM and then levels slowly return towards the ambient background levels, reaching a low again at around 3 AM.

This behaviour is characteristic of a vehicle-derived pollutant, the peaks occurring at the

times of peak traffic flow such as London Haringey; morning and evening rush hours. In the cases where the levels are maintained throughout the day; such as can be the case at London Bloomsbury (Oxford St) this is due to the type of traffic (restricted to buses, taxis and H/LGV) and the nature of this traffic, i.e. constantly high flows are maintained throughout the day (QUARG 1996).

Summer smog events are associated with anticyclonic conditions, light winds, high temperatures and clear skies (or strong sunlight). Winter smog events are associated with anticyclonic conditions, low to light wind speeds, low temperatures and shallow mixing depths. The common factors in both cases are poor mixing and dilution of pollutants and a weather system that allows concentrations to collect.

5.3 Rural Particulate Concentrations

Generally speaking it is possible to say that PM_{10} concentrations are found to be in the following order of magnitude: URBAN ROADSIDE > URBAN BACKGROUND > SUB-URBAN > RURAL. Black smoke measurement have tended to follow the same trends, with the exception that BS measurements have now become much closer in rural and urban sites due to the effects of the clean air acts of the fifties and sixties (QUARG 1996).

A study at Chew Lake, Bristol and Cardiff (International Mining Consultants Limited 1995 quoted in QUARG 1996) demonstrated that episodes of elevated PM_{10} at the urban sites were not reflected at the rural site (Chew Lake). A study in Canada (Brook J R *et al* 1997) concluded that ambient concentrations of fine and coarse (PM_{10} and $PM_{2.5}$ respectively) were higher in urban than rural areas, they also noted a correlation to SO_4^{2-} indicating a link with fossil fuel combustion. However, as King A *et al* (1997) and Steadman (1996) reported (see below) in cases of transboundary pollution events these distinctions can become obscured.

5.4 Transboundary Particulate Pollution

It was reported in Atmospheric Environment (King A *et al* 1997) that;

- The majority component of PM_{10} particulate matter, in both urban and rural locations, is generated outside of the immediate area.

- Elevated concentrations are generally associated with air masses arriving from continental Europe.

- Exceedance of air quality guidelines is predominantly linked to national and tran-boundary phenomena, rather than local emissions.

Their conclusions were based on the events of two periods of persistently high PM_{10} concentrations seen across the Automatic Monitoring Network (AUN) in the UK. The first event took place from 19 January to 4 February 1996 the average concentration over twelve of the AUN sites was 43 $\mu g\ m^{-3}$ with six exceedances of the 50 $\mu g\ m^{-3}$ National Air Quality Strategy (NAQS) limit. The second was from the $_{10}$ to 25 March 1996 when there was a countrywide average level of 57 $\mu g\ m^{-3}$ and eleven cases of NAQS exceedance.

During the first case there were pure easterly winds, which were bringing air from mainland Europe, and the episode ended with pure anticyclonic conditions. Concentrations in Ystradowen (site of rural TEOM in south Wales) closely reflected the concentrations countrywide. Localised contributions could be seen to cause a small increase at twelve urban sites, demonstrating a well-established ambient component.

Steadman (1996) also considered the March episode and noted that there were no significantly elevated levels of NO_x associated with this event, this being a good indicator of traffic related pollution events he concluded that there was no significant primary traffic contribution. He also noted high concentrations of secondary sulphate and nitrate particulate at three rural sites, and blanket concentrations at rural, city and city centre sites which

tended to obscure the diurnal variations at all but the London Bloomsbury site. This pattern makes a very strong case for the input of transboundary particulate pollution being the cause of a countrywide pollution event.

5.5 Traffic Influences

Roadside sites of the AUN repeatedly show elevated levels of PM_{10} higher in comparison to urban background and suburban sites (Broughton 1997). QUARG (1993a) reported 4 roadside sites with M-type samplers (cut point ≈ 10-15 μm AD) as having concentrations in the order of $_{2.5}$ to 3 times higher than city centre sites. The AUN site at Marleybone, Oxford Street, London displays some of the highest levels in London, this is due not only to its proximity to a consistently high flow of traffic, but also to the fact that the traffic is restricted almost exclusively to diesel vehicles which are known to emit higher levels of particulates than petrol vehicles (QUARG 1996 and QUARG 1993b). Harrison and Jones (1995) (quoted in QUARG 1996) monitored PM_{10} levels at a city centre site and in close proximity to the A38 using AUN TEOM systems from Sept. 7-30 1994. They found that the A38 site had levels averaging 45.5 μg m^{-3} where the city centre site averaged 25.4 μg m^{-3}, representing a 79% increase at the A road site. The Chew Lake study mentioned above (International Mining Consultants Limited 1995 quoted in QUARG 1996) found concentrations at 63% of those found in Cardiff and Bristol. Further they found that the chemical constituents of the rural PM_{10} contained 30% vehicle derived constituents.

It is widely accepted that traffic makes a major contribution to the urban aerosol. The diurnal patterns (Broughton 1997) described above are very much an indicator of this situation. Another strong indication of this are the positive correlations found between NO_2, CO and PM_{10} concentrations in the urban atmosphere (QUARG 1996).

6. SAMPLING OF THE AMBIENT AEROSOL

There are four main objectives that may be accomplished through the monitoring of ambient aerosols:

- To determine ambient concentrations
- To determine compliance
- To identify components
- To appoint sources

In order to achieve any of the above reliable and well-defined systems must be used for the sampling procedure. This requires the following criteria to be met:

- Well defined fractions must be collected
- On sampling surfaces that are inert
- Using inert, suitably compatible filter media
- A sufficient deposit must be collected to ensure accurate analysis

In this chapter some of the more common methodologies will be considered. Table one shows the most common systems applied to the monitoring of particulate loadings in the atmosphere.

Table 1: Common methods of particulate monitoring.

METHOD	FRACTION
REFLECTANCE	BS
GRAVIMETRIC	TSP, PM_X, Others
BETA ATTENUATION	Generally PM_{10}
LIGHT SCATTERING	SPM, Other

6.1 Filter Based Methods

Filter based methods all incorporate a pump, a filter and housing and a method for recording the volume sampled. The simplest of these is the total suspended particulate (TSP) or suspended particulate matter (SPM) method which is described below. More sophisticated systems are available now which incorporate size selective inlets, flow control systems, accurate volumetric recording and even incorporate the logging local meteorological perameters such as temperature, pressure and wind speed and direction. These modern systems can be programmed for sophisticated sampling regimes or in some cases can give near real time results with a high temporal resolution.

6.1.1 Filters and Filter holders: Some Considerations

All of these methods require the use of filters, which must be weighed before and after sampling, the difference giving the particulate mass collected. This procedure requires time, resources and the use of suitably sensitive balances, with each repeat weighings after 24-hour acclimatisation periods (in conditions of controlled temperature, humidity and ambient particulate levels to ensure the accuracy of results). The finer the cut point of the sampler becomes, the more stringent the overall procedure must become as aresult of the reduced sample size.

The interlab comparisons conducted for the PEACE study showed a small positive trend in the consecutive weighing of several filter types at the five labs (Hoek G *et al* 1997). This was interpreted as being due to repeated handling and was considered as being of little significance to overall PM concentrations. However, this does serve to show how the most stringent of measures must be taken to avoid errors.

The USEPA specify that three conditions must be met by filters used for compliance PM_{10} monitoring in the US (Keith 1996):

- 99% collection efficiency must be met
- Weight loss and gain, due to chemical and physical instability, must represent less than 5 $\mu g\ m^{-3}$
- Alkalinity must ensure that SO_2 and NO_x absorption is avoided

Common filter types used are teflon membrane, teflon coated glass fibre, cellulose fibre, glass fibre, quartz fibre, etched polycarbonate membrane and nylon mesh or membrane. All of the above are suitable in certain conditions but some are more prone to static charging and some have hydroscopic properties, potentially causing problems with the weighing procedure (*personal experience*). Also when choosing suitable filters price and blank chemical constituents are important considerations, i.e. glass fibre may not be suitable for metals analysis due to high metals content.

When attempting to meet the 99% collection efficiency criterion the pressure drop across the filter must be considered. Too fine pore sizes in etched membrane filters are likely to put too much strain on the pump and may clog easily. A suitable pilot study will ensure that these problems are overcome.

Filters and their holders must always be protected from contamination during the sampling procedure. This may require the loading of filters into their holders to take place under clean room conditions and double bagging during transportation (Ms A Wheeler *pers. Comm.*).

Filter holders must provide a homogenous deposit if there are any chemical analysis of filters being undertaken. They must mate to the sampler without leaks, be inert to gases to avoid filter artefacts. There must be a low-pressure drop across the empty holder in the sampler to avoid any interference with flow rates. Finally they must be simple, durable and cheap (Keith 1996).

6.1.2 *Effects Of Humidity*

Humidity and temperature effect the weight of filters and samples, depending on the hygroscopic properties of both. As the particulate levels being monitored are minute this often effects the results. All filters and samples are therefore conditioned to a standard humidity and temperature.

With respect to ambient aerosols, electrolytic material will increase in mass and size with increases in relative humidity (RH). Hitzenberger R *et al* (1995) showed, by the re-weighing of impaction foils from a previously sampled aerosol at various RH's, that the bulk of such material was to be found in the accumulation mode and therefore this was the fraction that showed the greatest mass increase factor (wet mass/dry mass). Mass increase factors of 3.9 were found at 95% RH for the 0.5-1.0 μm AD where as the 8.0-16.0 μm fraction showed a mass increase factor of 1.4 at 95% RH.

Busch B *et al* (1995) showed that the diameter of a monodisperse NaCl or KCl aerosol changes diameter at a given RH. The different growth curves are the result of the thermodynamic properties of the salt in question, NaCl shows a growth factor of 1.75 at around 73% where KCl has a growth factor of 1.8 at around 84%. It is worth noting the abrupt change in diameter at a given RH and the individual salt's growth point, this will effect the changes in overall size distribution of ambient aerosols at lower levels of RH.

Busch B *et al* (1995) also showed that the submicron fraction of an ambient aerosol displayed distinct hydrophobic and hydrophilic fractions, reflecting the complex composition of airborne particulate matter.

6.2 The Open Faced Filter Methodology

Total Suspended Particulate (TSP) is monitored using a variety of systems but all tend to use the same basic components. A medium to high volume pump is used to pull air through an open-faced filter (Figure 5) and the volume of air is recorded using a gas meter. One example of such a system is that used for this study; the Rotheroe and Mitchell L30 and

L100 pumps, these incorporate an open-face filter housing on the body of the pump and a flow meter. The volume sampled can be estimated by taking the average of initial and final flow rates and multiplying by the sample duration. It is also possible to fix the filter housing remotely and place a gas meter behind the filter to obtain more accurate sample volumes and facilitate the inlet siting.

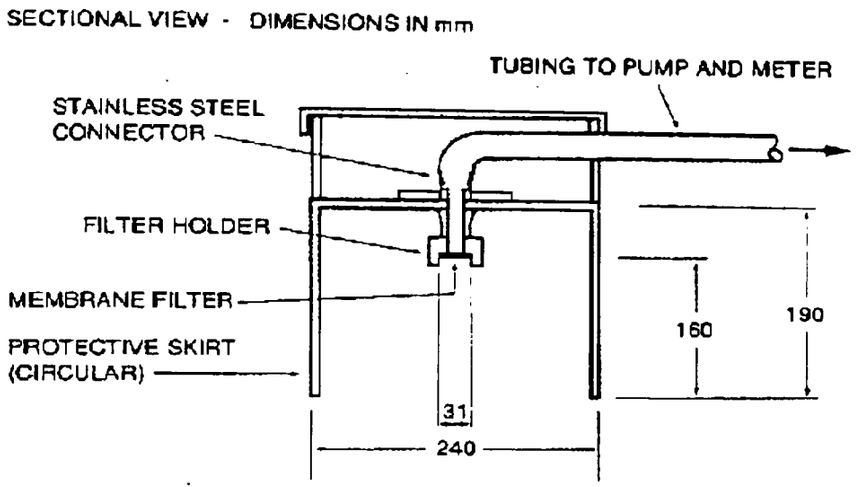


Figure 5: A sectional diagram of an open-faced filter holder similar to that used in this study for TSP monitoring (ignore dimensions). (QUARG 1996)

This method can easily be arranged in such a manner as to ensure large enough samples to allow for relaxed control of particulates during the weighing phases and a five figure balance should suffice for analysis. It is a reasonable cheap and simple method, which requires little specialist knowledge or equipment.

The main disadvantages are the time it takes for the analysis of results and therefore their presentation and the question of what the results indicate in pollution or health terms. The measure, TSP, contains all suspended material beyond that which is inhalable and is a mixture of naturally and anthroprogenicaly sourced material. This means that in terms of a pollutant its effects are masked by the inclusion of material that is naturally occurring and can't be easily controlled and by the inclusion of a fraction which has little effect on health.

6.3 Cascade Impactors

Cascade impactors separate the aerosol into different fractions depending on their aerodynamic diameter. This is done by forcing the airflow through progressively smaller holes and through progressively smaller gaps (S,T and W in Figure 6), which operate as a sequence of pre-seperators for the next stage. In each case the air stream contains the fraction below the cut off point of the stage above, the air stream velocity is increased by forcing it through smaller holes, the inertia of the particulate matter is increased and by decreasing the gap between the inlet and the impaction surface the curvature of the air flow is sharpened therefore the cut point is decreased. The heavier particles in each stage are impacted due to their inertia on a filter or collection surface, a back up filter collects everything in the fraction bellow the final stage (see Figure 6). The fraction's mass are either determined gravimetricaly or in real-time if using crystal based equipment.

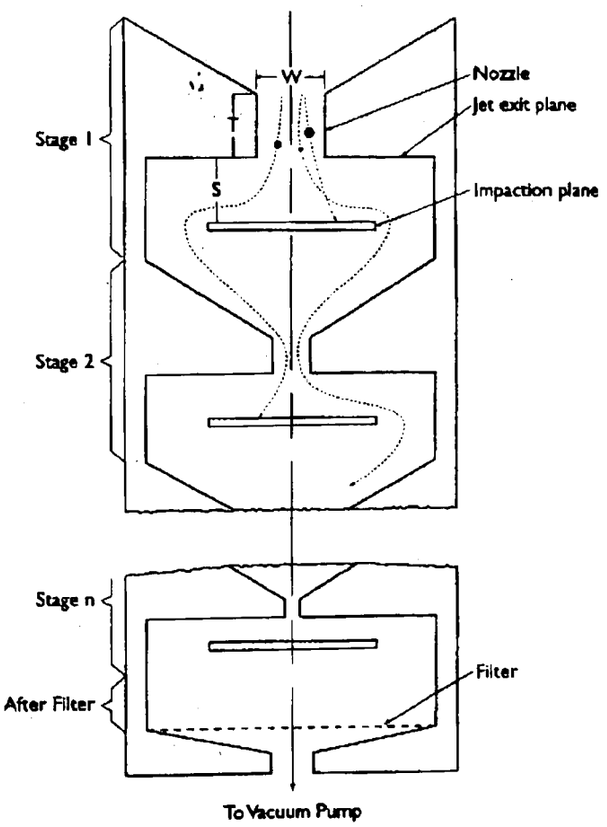


Figure 6: schematic diagram of a cascade impactor (Wilson R and Spengler J D 1996)

The outstanding advantage of a cascade impactor is the ability to provide information on the size distribution of a given aerosol, the prolonged use of such an instrument could give information on the changes in this distribution which may or may not be reflected in the overall measurements being taken. Another advantage is the speed of results; gravimetric based systems will require the weighing procedure and are therefore no faster than other methods but crystal based systems offer the capacity to have data sets within 15 minutes (depending on the ambient concentrations). Such systems can be of great use when initially investigating a site for the preparation of a sampling project.

The disadvantages of these systems are the time delay in obtaining results (if the system is filter based), the need for experienced operators as cascade impactors are precision equipment and require precision methods, and the generally low resolution of the results.

6.4 Beta Attenuation Monitors (BAM's)

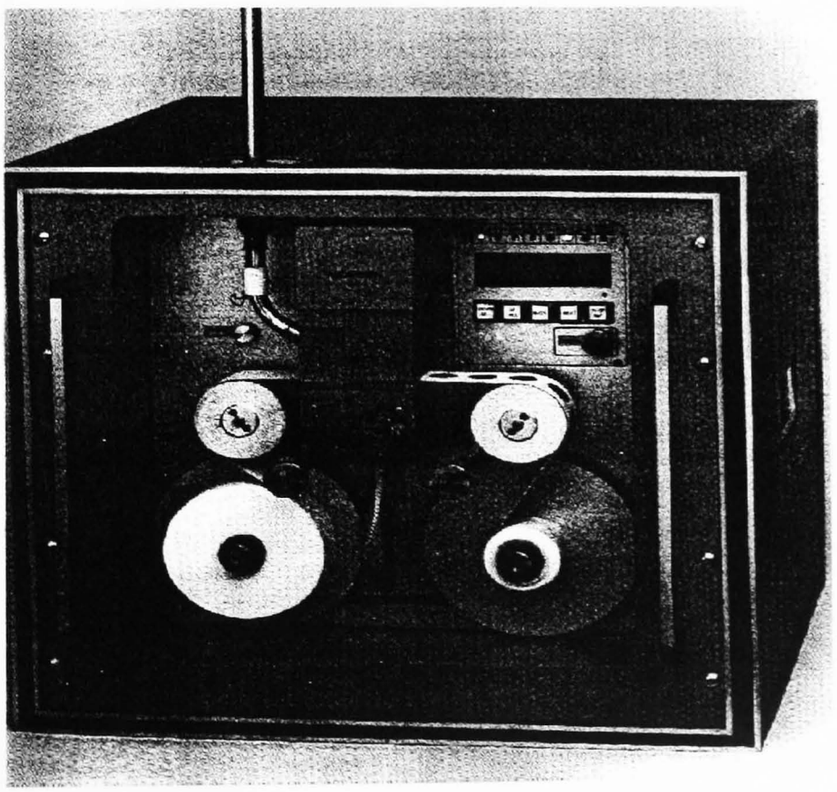


Figure 7: A Graseby-Anderson beta attenuation monitor, the inlet is a typical PM_{10} impaction inlet. (source Keith 96)

In a study in Taiwan (Tsai C J 1993) an ASI/GMW model 1200 and Wedding HVPM$_{10}$ samplers, Kimoto model 185 and Wedding BAM were collocated at three sites and their performance compared. It was found that the Kimoto BAM produced scattered results (possible re-entrainment of particles in the cyclonic preseperator). The Wedding BAM was found to be stable and well calibrated. This illustrates that the entire system must be robust for any sampler to operate accurately, given this BAM are reliable instruments.

6.5 Tapered Element Ossilating Microbalance (TEOM)

The Tapered Element Oscillating Microbalance or TEOM monitor is the favoured instrument of the UK AUN. It is an USEPA reference method made by Ruprecht and Patashnick, fitted with their standard PM$_{10}$ head as standard, it will also accommodate PM$_{2.5}$, PM$_1$ and TSP heads. Figure 8 shows the schematic diagram of the TEOM.

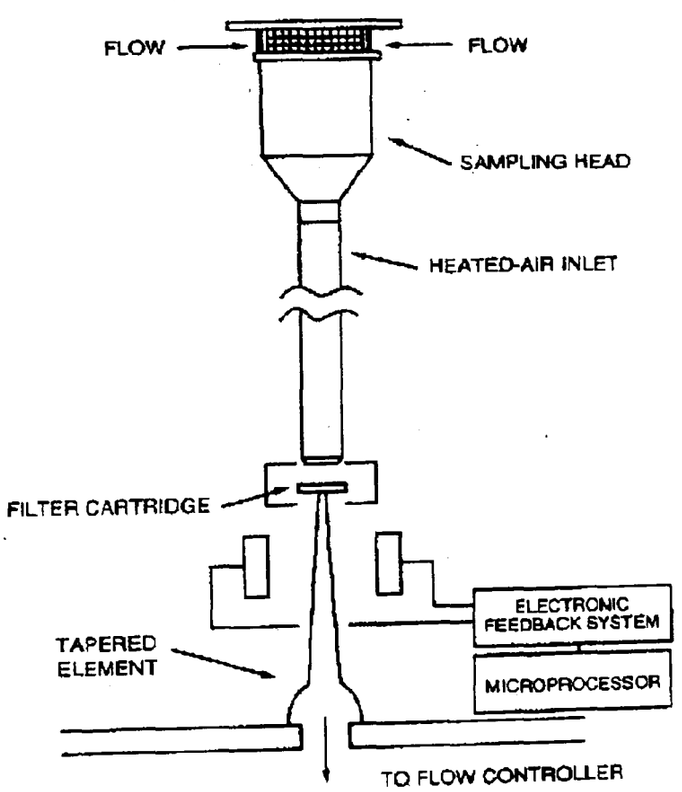


Figure 8: Schematic diagram showing the sampling and operating principals of the TEOM ambient aerosol monitor (source QUARG 1996)

The basic principle of the TEOM is that the resonant frequency of the tapered glass element is dependant on its mass, the filter is physically attached to this element and so any increase in mass is reflected in a change in frequency of the element. This is detected and translated into mass increase by comparison with standards.

The system takes sample air in at 16.7 L min^{-1} to achieve the cut-point of the inlet, and splits the flow in order that the filter receives 3 L min^{-1}. The post selection inlet is heated to 50^{O}C to drive off any moisture, as there is no acclimatisation of filters and sample mass. This can result in the volatilisation of VOCs, and subsequent under sample. The system offers near real time analysis, giving 15-minute averages and has proved to be a robust instrument.

6.6 Optical Systems

Optical analysers can utilise the light-scattering properties of particulates to measure concentrations. The response of such instruments is very much dependent on the size distribution of the aerosol, shape and refractive index of the particles. As a result, they tend to be more effective in industrial scenarios where the aerosol is well defined and relatively stable in terms of composition.

These types of systems can be fitted with size selective inlets, before the sample is fed to a light scattering chamber to be analysed. They can and are used as ambient monitors with one of their advantages being the speed of results (real time).

However, in ambient circumstances their performance is very much dependant on their calibration. They are calibrated with test dust of known distributions for accurate results. Under ambient conditions the nature of the aerosol can change rapidly and little is known about how much this varies from hour to hour, or how the calibrated instruments cope. QUARG 1996 recommends that these instruments are treated with caution.

7. FACTORS AFFECTING THE PERFORMANCE OF SAMPLING SYSTEMS

More sophisticated methods for the monitoring of particulate matter have evolved in response to the need to understand the size distributions of aerosols and to measure a fraction or fractions that are more significant in terms of related health effects. The ability to monitor these distinct fractions accurately requires an understanding of the system being used and the potential shortcomings of that system. Also the availability and use of cheaper and more compact systems requires enough knowledge of the factors effecting the performance of all monitors so that the results can be compared realistically with those available from other sources of information.

7.1 Isokinetic Sampling

When air is being drawn through a sampler inlet the sample being collected is automatically corrupted. This is due to the instability of the air being sampled, i.e. it has its own free stream speed and this has imparted momentum, velocity and direction to the particulates suspended in it (Figure 9**(a)**) (Colls 1997). As air is drawn into the inlet (given that the inlet happens to face directly into the wind) there are three basic scenarios. First the sampler may draw in air at a rate below that of the free stream (Figure 1**(c)**), in this case some of the particles may be carried around the samplers inlet by the differential pressure (higher round the inlet than through it), however large particles with a large inertia may continue into the inlet. In the second case the sampler is sampling at a rate which is faster than the free stream speed of the aerosol (Figure 1**(e)**), in this case air from around the inlet is drawn into the sampler carrying those particles lacking the inertia to escape (the finer particles) the larger particles with enough inertia will carry on in the same direction as their stream lines. In the third and perfect case the sampler draws air in through an inlet facing directly into the wind at the same rate as the free stream speed, this is known as isokinetic sampling (Figure 1**(d)**).

It is clear that the above scenario for isokinetic sampling can never be met in ambient air monitoring. However, the problem can be partially overcome by careful design of the inlet to the sampler, a horizontal orientation of the inlet orifice and a rain cowl are common features of compliance monitor inlets, this ensures that the inlet is always open to the direction of the wind.

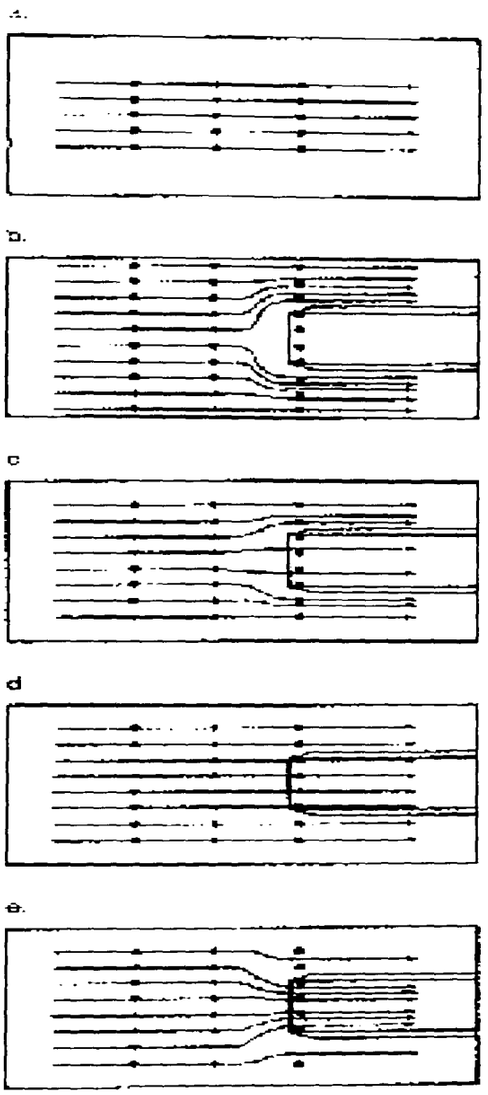


Figure 9: Flow stream lines and the corresponding particle behaviour for moving air and a sample inlet under the following conditions: (a) No inlet; (b) Inlet not sampling; (c) Inlet speed lower than sample speed; (d) Isokinetic sampling at the free stream speed; (e) Inlet speed greater than free stream speed (source Colls 1997)

7.2 Pre-separators

These systems require the use of pre-separators to exclude any particulate that exceeds the required size fraction, common separators operate on the principals of direct impaction, virtual impaction, cyclonic flow, selective filtration and elutriation (Keith 1996). As most monitoring uses physical methods to pre-separate and collect samples, each sampler will have its own unique characteristics. Given that (in the case of PM10) the samples collected are in themselves defined by the sampler used and the levels are reported as PM10, the US Environmental Protection Agency (EPA) have designated certain sampling systems as reference methods. These methods meet the criteria set by the EPA and are deemed to be collecting the same fraction: <10μm AD.

7.2.1 Impaction seperators

Impactors use the inertia of particles to provide a cut-off point at a given aerodynamic diameter. This is achieved by controlling the flow rate and impacting the air stream onto an impaction surface which may or may not be greased to improve the impaction efficiency (i.e. avoid particle bounce). This device can be used as a sampler in its own right, collecting the fraction impacted, or as a pre separation device for monitors. In the latter case the impactor is used to remove particulates over a certain size (i.e. PM_{10}) allowing everything below that size to be collected on a filter.

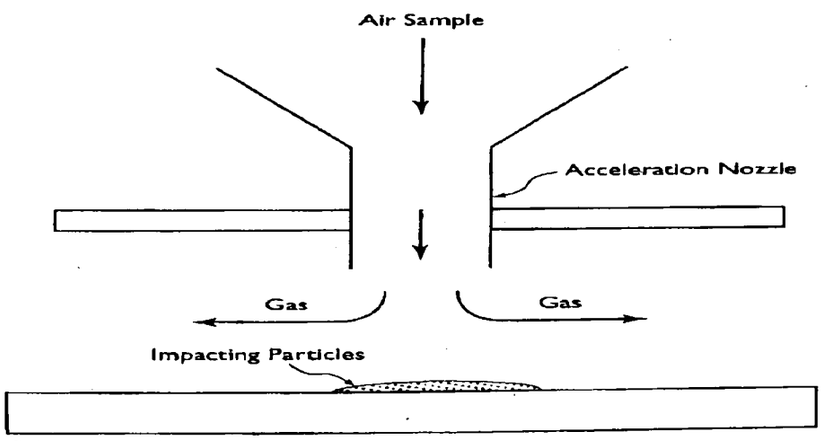


Figure 10: A schematic of the impaction system. (Wilson R and Spengler J D, 1996)

on TEOM monitors to provide the cut point for compliance monitoring in the UK and the USA (EPA designated). It is also used as the PM_{10} inlet on the Partisol 2000 used in this study. It incorporates the vertical orientation of inlet and rain cover, the jar to the right is used to collect any excess rain drawn into the impactor. The efficiency curves demonstrate that the fraction collected is reliable in terms of the thoracic and PM_{10} convention curves, across a reasonable range of wind speeds.

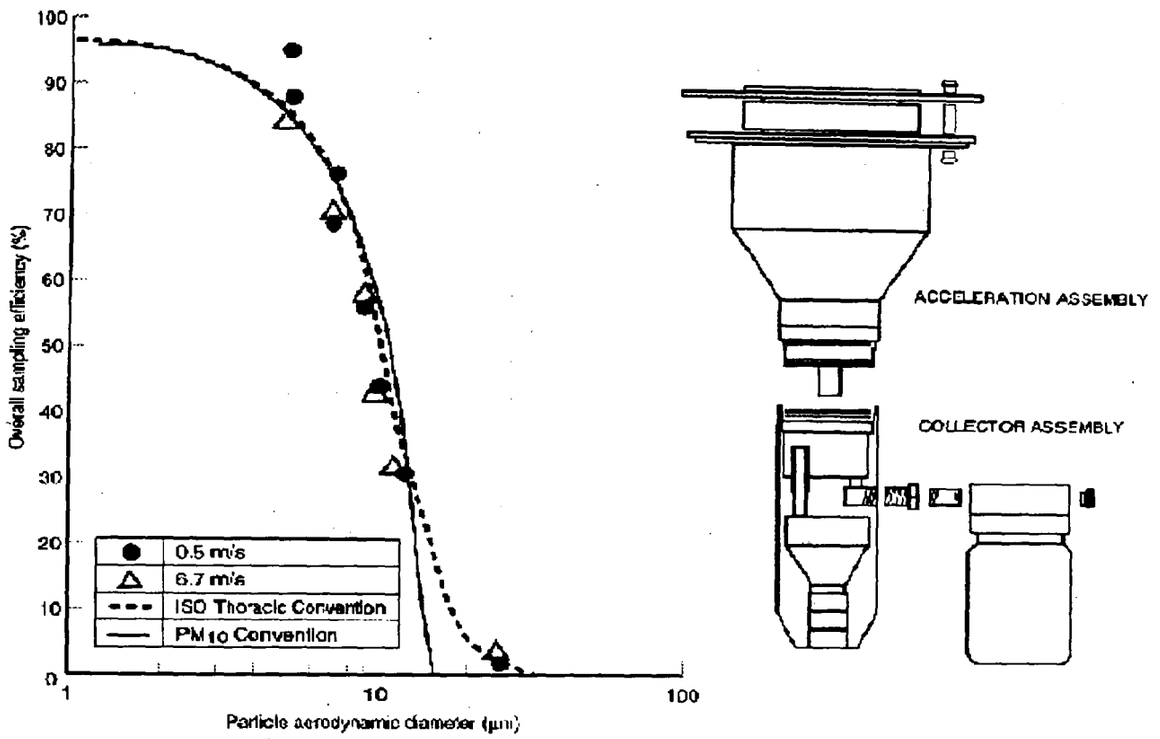


Figure 11: A typical impactor based PM_{10} size selective inlet, as used on TEOM and Partisol 2000 systems with efficiency curve, experimental data and a thoracic convention curve (source QUARG 1996)

The advantage of this system is that the tried and tested technology is very predictable, it is relatively cheap and can be used on small to large scale samplers. The virtual impactor has the advantage that it separates the fine and course fractions, which can then be analysed separately. The disadvantages are: sampler heads made with poor quality control resulting in poor precision between heads, impaction plates often require cleaning with solvents and re-greasing over relatively short sampling periods (days) and in some cases can be bulky.

Interlab comparisons during the PEACE study reported variations of up to 50% between some designs (Hoek G *et al* 1997). This is explained by the differences in greasing procedure (or lack of) and as a result of design parameters and tolerances.

7.2.2 Cyclonic seperators

Cyclonic separators operate on the same principal as industrial cyclones. The difference in this case being that where the latter are designed to extract as much of the aerosol as is possible, cyclones are designed to provide a strict cut-point, bellow which particles continue to the filter.

Again the cyclone operates on the basis of inertia; decreasing the diameter of the inlet pipe accelerates the sample stream, increasing the inertia of the particulates. The sample stream is then introduced to the top wall of a conical chamber, the stream is drawn into a vortex, down the chamber and back up through the centre in a very fast spiral flow. During this process the particles above a certain mass will be ejected from the stream due to the excess inertia, these impact on the side walls and are collected at the bottom of the cyclone.

7.3 Inlet Efficiency

Each inlet is characterised by its efficiency curve, these curves are generated in a wind tunnel using an aerosol of spherical particles of unit density. The particles that penetrate to the filter are measured and counted. A curve is plotted of particle diameter against percentage (of the original concentration in the tunnel) penetrating, the diameter at which only 50% of particles penetrate (d_{50}) is the characterised cut point of the inlet (Keith 1996). The US Environmental Protection Agency (EPA) have a criterion that the efficiency curve of a given inlet must be such that: the mass of any sample from a given aerosol fall within 10% of that expected from an ideal sampler, i.e. one with an efficiency curve based on lung deposition (American Conference of Governmental Industrial Hygienists 1988). This is intended to ensure that any oversample of the more coarse fraction is sufficient to compensate for the accompanying undersample of the fraction being monitored

7.4 Particle Bounce

Particle bounce is literally where solid particles bounce from surfaces intended to trap them and therefore impede their passage onto a filter of collection substrate. This can occur in all inlet types, but is possibly most important when considering impaction systems. It has been shown by Wang and John (1987) (quoted in American Conference of Governmental Industrial Hygienists 1988) that the fraction of particles which bounce (FOB) is mostly a function of the kinetic energy of the particles. This means that the probability of bounce increases with AD, and this was shown to be the case with bounce increasing rapidly beyond a certain particle size depending on the criteria.

The USEPA have a criterion that requires samplers to sample solid particles of 20 μm AD with no more than 5% more efficiency than of liquid particles of 20 μm AD (American Conference of Governmental Industrial Hygienists 1988). Wang and John (1987) (quoted in American Conference of Governmental Industrial Hygienists 1988) showed that this criterion may still result in up to 20-30% oversample, a 5% criterion for 50μm AD should reduce the oversample to less than 10%. This type of consideration is generally important as high levels of particle bounce will result in overestimations of ambient loadings in dry conditions and specifically important in cascade impactors as bounce will result in completely erroneous results.

The USEPA established the Phoenix study to investigate this problem in two samplers that were designated USEPA standard methods (American Conference of Governmental Industrial Hygienists 1988), the Sierra Anderson SA 321A and a Wedding hi-vol PM_{10} monitor. These samplers were collocated, in an area and conditions affording large wind blown particles, with a Sierra Anderson Dichotomous sampler SA 246B and a Wedding Dichotomous sampler GMW-9200. By using the principle of virtual impaction the dichotomous samplers eliminate bounce. The results showed that The SA 321A was oversampling with reference to the SA 246B and GMW-9200, whilst a second SA 321A with oiled impaction surfaces showed less than 10% difference. A second Wedding sampler

was given light cleaning between runs, again this improved accuracy. The conclusions drawn were that oil suppresses bounce and that loose, impacted particulate can be re-entrained if allowed to collect.

7.5 Flow Control

As the inertia of a given particle depends on its velocity, the efficiency of a pre-separator is dependent on flow-rate. Many modern sampling systems utilise flow control systems to guarantee a reliable cut-point during sampling. Typical systems are described below

7.5.1 Manual Volumetric Control

The flow rate is set manually at the start of sampling, given a suitable filter and flow rate the pressure drop across the filter will remain constant throughout sampling despite loading. The flow rate can be expected to drop by < 10% in a 24 hour run if ambient concentrations are < 200 $\mu g\ m^{-3}$ (Keith 1996). A suitable pilot study incorporating the monitoring of flow rate at the start and end of each sample run will verify this.

7.5.2 Automatic Mass Control

This system uses a thermal anemometer to detect the flow in the sampler. If the flow rate moves outside of pre-set tolerances the motor speed is adjusted to maintain a mass flow per unit of time. This system allows for the compensation of ambient pressure and temperature changes as flow is maintained on a mass basis (i.e. the mass of one m^3 of air at 1 atmosphere and 20°C). This is considered valuable as Wedding estimated a 10% variation in mass and volumetric measurements due to variations in temperature and pressure (quoted in Keith 1996). Systems such as these need recalibrating seasonally and at differing elevations.

7.5.3 Differential Presure Control

In this system a diaphragm valve is placed between the filter and an orifice, this can be used to maintain a constant pressure between the filter and the orifice. When the pressure drop

increases due to loading of the filter, the diaphragm can be opened to maintain pressure and therefore the flow-rate is kept constant. A differential pressure control system is used on the Grasbey-Anderson dichotomous sampler (Keith 1996).

7.5.4 Critical Oriffice or Throat Control

A very precisely sized opening can be placed between the pump and filter in this system. If the pressure drop after the filter is over 53% of the pressure upstream of the orifice a constant flow will be maintained. This system requires large pumps and is restricted to low flow rates in the region of 20 l min^{-1} (Keith 1996). Figure 12 shows a Wedding and Associates sampler that utilises this system of flow control.

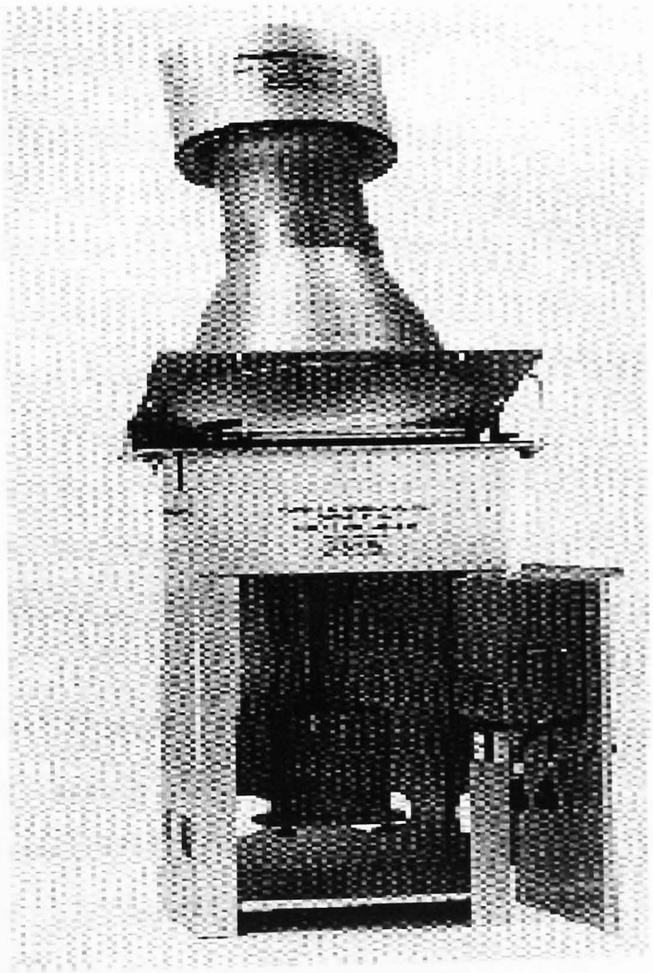


Figure 12: A Wedding and Associates critical flow high-volume sampler with a PM_{10} inlet,
(this sampler utilises a critical throat flow control system: source Keith 1996)

8. RELATIONSHIPS BETWEEN THE FRACTIONS TO BE MONITORED

It has been shown in earlier chapters that particulate concentrations are Affected by meteorological conditions and the seasonal changes. This is truer of the coarse fractions (Harrison *et al* 1997 see Figure 3) due to the effects of resuspension and deposition rates. Generally speaking it is evident that the coarser fractions result from mechanical sources and the finer from combustion and secondary sources (QUARG 1993, QUARG 1995). It therefore follows that the relationships between the fine fractions; PM_{10}, $PM_{2.5}$ and PM_1 will be more closely related, especially when monitoring in proximity to a combustion source such as a road.

8.1 Summer Relationships at Archway Road

A previous, un-published study was undertaken at the same site on Archway Road during 29/06/98 to 08/09/98. Regression analysis was carried out on all possible combinations of those fractions which were monitored as 24-hour averages, the results can be found in

Table 2. No clear relationships were found between TSP and the other fractions. This is as would be expected, TSP being influenced most strongly by meteorological factors including wind speed, direction and rain.

PM_{10} correlated well with the two finer fractions, slightly better with $PM_{2.5}$ than for PM_1 as these two fractions are less influenced by meteorology. Average $PM_{2.5}$ correlated better with PM1 than the two collocated $PM_{2.5}$ samples. This probably reflects short-term differences in levels between the two $PM_{2.5}$ sampling periods (5 minute sequences across four heads) and errors due to gains and losses in the process of transportation and weighing. Average $PM_{2.5}$ may have smoothed out some of these errors and resulted in slightly better correlations between this and the other PM fractions.

Table 2: Regression relationships between the fractions monitored at Archway Road (using 24-hour mean concentrations)

FRACTIONS	REGRESSION EQUATION	R^2 VALUE
$^{P}PM_{10}$ Vs $^{A}PM_{10}$	$^{P}PM_{10} = 1.034\ ^{A}PM_{10} + 1.944$	0.79
$^{(1)}PM_{2.5}$ Vs $^{(2)}PM_{2.5}$	$^{(2)}PM_{2.5} = 1.042\ ^{(1)}PM_{2.5} - 0.715$	0.857
$^{P}PM_{10}$ Vs $^{P}PM_{2.5}$	$PM_{2.5} = 0.76\ PM_{10} - O.294$	0.823
$^{P}PM_{10}$ Vs $^{P}PM_{1}$	$PM_{1} = 0.673\ PM_{10} - 0.773$	0.755
$^{P}PM_{2.5}$ Vs $^{P}PM_{1}$	$^{P}PM_{1} = 0.859\ ^{P}PM_{2.5} - 0.169$	0.873
$^{A}PM_{10}$ Vs $^{P}PM_{2.5}$	NOT REPORTED	0.819
$^{A}PM_{10}$ Vs $^{P}PM_{1}$	NOT REPORTED	0.775
TSP Vs $^{P}PM_{10}$	NOT REPORTED	0.047
TSP Vs $^{P}PM_{2.5}$	NOT REPORTED	0.065
TSP Vs $^{P}PM_{1}$	NOT REPORTED	0.106
TSP Vs $^{A}PM_{10}$	NOT REPORTED	0.05

All values are in $\mu g\ m\text{-}3$ ^{A} = Air Metric ^{P} = Partisol 2000

The strongest correlation was between $PM_{2.5}$ and PM_{1},. This could be expected as the two are very similar; with PM_{1} representing the nucleation and accumulation modes and the $PM_{2.5}$ being dominated by these modes (QUARG 1995 and others). shows the summary statistics for the same summer sampling period. The summary statistics for PM_{10} showed that levels were consistently lower than the legislated limit of 50$\mu g\ m^{-3}$ (as a 24 hour rolling average) throughout the monitoring period, on average levels were at 42% of the limit. The percentage contribution of $PM_{2.5}$ to PM_{10} was found to be 76%. During this study $PM_{2.5}$ ranged from 100% (31/07/98) to 60% (30/07/98) of PM_{10}.

Table 3: summary statistics for fractions monitored at Archway Road between 29/06/99 and 08/08/99: showing results for all data, week days and week ends.

DATA SET	STATISTIC	OPEN FACED			PARTISOL 2000			AIRMETRIC MINI-VOL	
		TSP_{AM}	TSP_{PM}	TSP	PM_{10}	$(AVE)PM_{2.5}$	PM_1	$A\ PM_{10}$	$A\ PM_{10}$ (RH)
	N	40	42	37	34	33	34	42	17
ALL	MEAN	35	45	23	21	16	13	24	29
DATA	STDDEV	18	21	15	6	5	4	7	5
	STD ERROR	2.8	3.2	2.4	1.0	0.9	0.7	1.1	1.2
	MAX	111	125	73	36	26	21	51	34
	MIN	15	11	8	11	7	4	13	21
	N	29	30	28	25	24	25	30	14
WEEK	MEAN	33	47	22	21	16	13	24	29
DAYS	STDDEV	10	22	13	4	4	4	7	5
	STD ERROR	1.9	4.0	2.5	0.8	0.8	0.8	1.3	1.3
	MAX	61	125	47	31	26	21	51	34
	MIN	20	11	8	14	9	6	14	21
	N	12	11	9	10	9	9	12	4
SAT	MEAN	42	39	27	21	15	14	24	30
SUN	STDDEV	26	15	19	8	6	5	8	5
	STD ERROR	7.5	4.5	6.3	2.5	2.0	1.7	2.3	2.5
	MAX	111	67	73	36	24	21	40	34
	MIN	15	21	10	11	7	4	13	23

ALL VALUES IN $\mu g\ m^{-3}$ N = NO. OF SAMPLES

Summary statistics indicated that the 24 hour Airmetric PM_{10} levels were consistently lower than the legislated limit of 50μg m^{-3} on all but one occasion (30/06/98) where the recorded level was found to be 51 μg m^{-3} (Partisol value 26 μg m^{-3}). The summary statistics showed the discrepancy between the two PM_{10} monitors to be 110%.

The means for all size-selective samples were considerably stable over week day and week end periods. The standard deviations and standard errors indicate more variability over the weekends and therefore less confidence in the means. This could be partly due to the smaller sample sizes, but may be a reflection of the traffic patterns on the road i.e. numbers of vehicles are fairly stable throughout the entire week. It is shown that the rush hours make a strong contribution to 24 hour concentrations throughout the week and weekend (non-rush hour mean was calculated to be 21μg m^{-3}).

The summary statistics for TSP show that during the sampling period and during weekdays the evening rush hour was making a large contribution to TSP levels with high average concentrations in this period. Over the weekends the morning rush hours had the highest concentrations. During the study those periods showing the highest concentrations were also the periods showing the most variance (STDEV), this reflects the variability of TSP levels with some periods showing very high results

8.2 $PM_{10}/PM_{2.5}$ Relationships From other Studies

A study in Birmingham (Harrison *et al* 1997) provided regression relationships for collocated PM_{10} and $PM_{2.5}$, these were monitored using TEOMs which are renowned for producing low results and the site was situated 70 meters from the elevated section of the M6, the results are shown in Table 4.

Table 4: Regression and correlation analysis for the Birmingham Hodge Hill site 1995 (Harrison *et al* 1997)

SEASON	REGRESSION RELATIONSHIP	R^2 VALUE
WINTER	$PM_{2.5}(\mu g\ m^{-3}) = 0.83\ PM_{10}(\mu g\ m^{-3}) - 2.92$	0.93
SUMMER	$PM_{2.5}(\mu g\ m^{-3}) = 0.42\ PM_{10}(\mu g\ m^{-3}) + 2.61$	0.62

WINTER = 01 OCTOBER 1995- 31 MARCH 1995 SUMMER = 1 MAY 1995 - 30 SEPTEMBER 1995

The weaker correlation for the summer period were explained in part by the greater production of secondary pollutants during the summer, and also by the elevation of PM_{10} during dry and windy periods, attributable to resuspension of road dusts, which was not matched by $PM_{2.5}$ concentrations (see Figure 3 andFigure 4). It was concluded that $PM_{2.5}$ represented around 80% of PM_{10} during the winter and around 50% of PM_{10} during the summer. Harrison *et al* (1997) also quote the work of Chow *et al* (1996), who's work in an American study found $PM_{2.5}$ contributions to PM_{10} to between 30 - 70%.

9. SITE DESCRIPTION

The monitoring site for this project is situated on the Archway Road (A1) on the outside balcony of The Winchester Hall Tavern. The A1 is a two lane red route at this stage and becomes dual carriageway two hundred meters further down the hill (south, see Figure 13). Further North west the A1 joins the M1 at junction 2. In the section between Archway underground station and Highgate underground station the A1 is a busy urban highway carrying buses, taxis, goods vehicles, local traffic and commuters (see Figure 13).

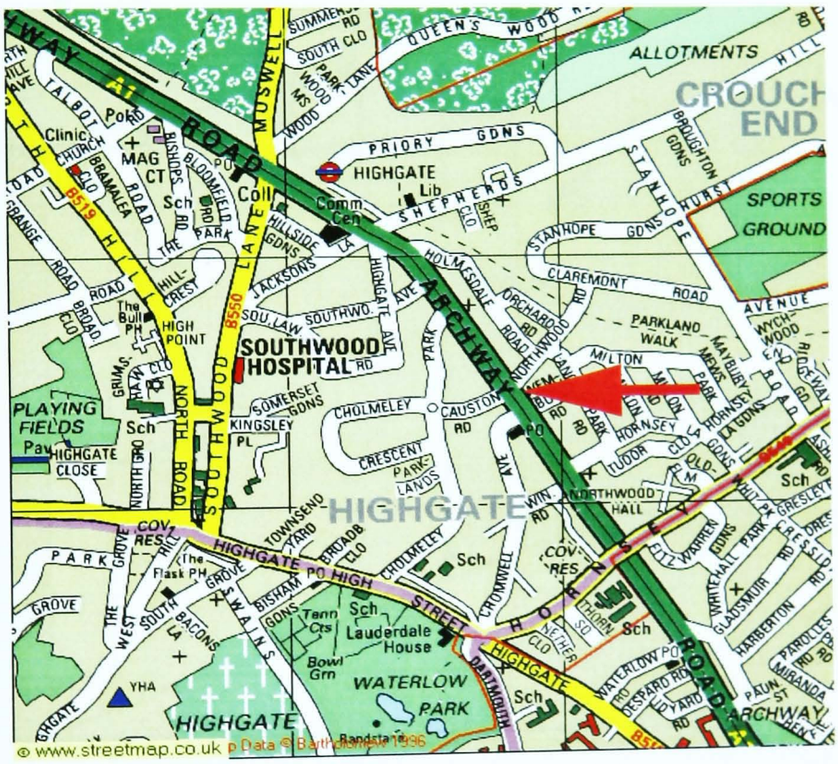
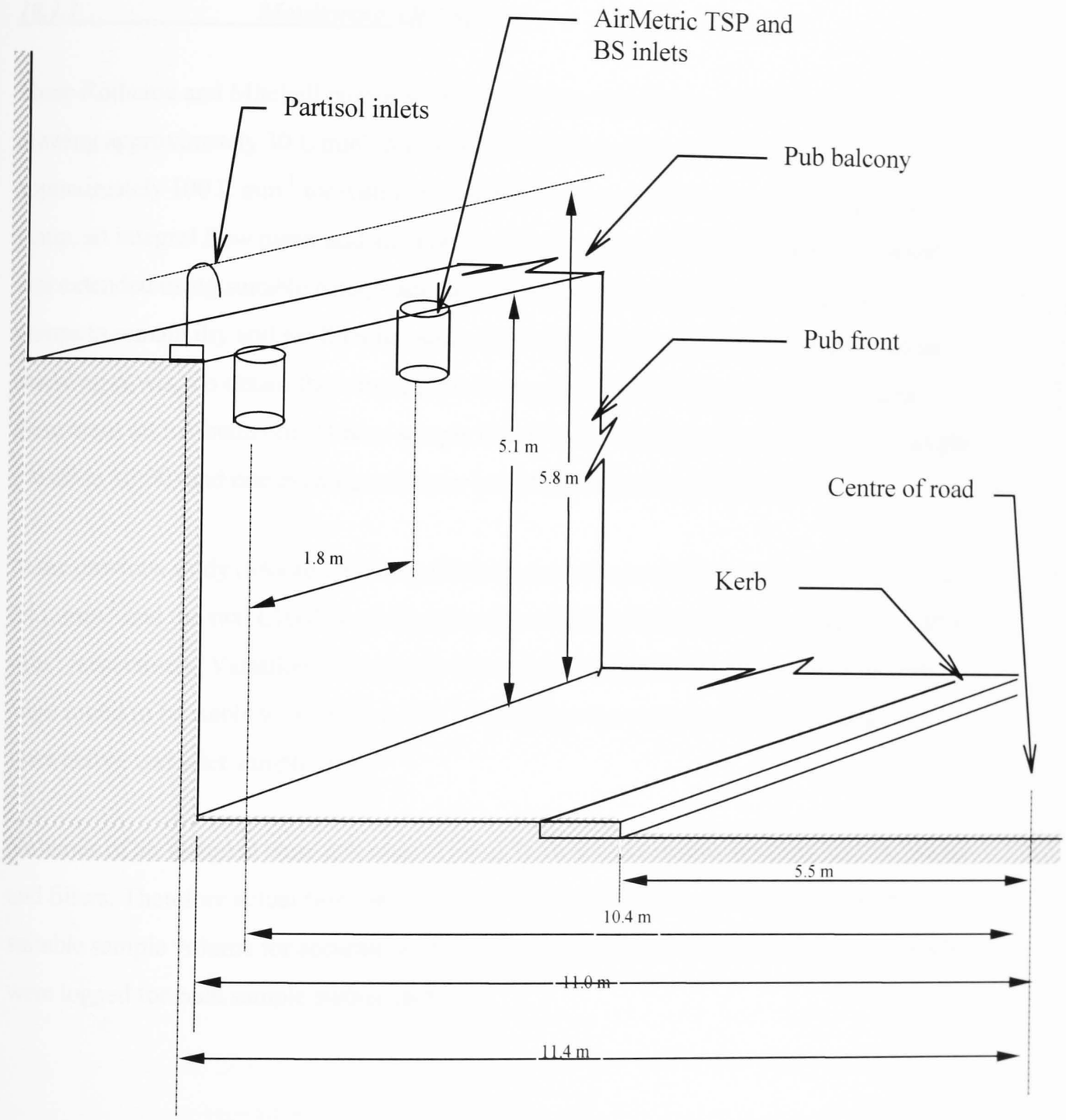


Figure 13: Site map showing the location of the sampling site on Archway Road (indicated by the red arrow).

The sampling site is at a height of ≈6 m above the street which in itself is at an elevation of ≈100 m on a hill roughly 70 m above central London, (OS grid reference 290877 sheet Landranger 176). The Partisol was seated on the balcony above and behind the AirMetrics and TSP inlets which will hang over the balcony 70 cm lower and 1 m further into the road. The entire sampling area will cover an area 1*1.8 m (see Figure 14).

Figure 14: Schematic of site at Archway Road.



10. METHODOLOGY

10.1 Equipment And Operating Conditions

10.1.1 Monitoring Of TSP

Three Rotheroe and Mitchell pumps were used for the monitoring of TSP. One L30, drawing approximately 30 L min^{-1} for 24 hour samples and two L100's drawing approximately 100 L min^{-1} for rush hour samples. These units consist of a high quality pump, an integral flow meter and an open face filter housing. The filter housing supplied was extended using suitable fittings and hose to be situated remotely, allowing for the pumps to remain dry and for filter housings to be mounted face to the street with weather shielding cowls. To obtain the sample periods required, 24 hour timers were employed, these were set to obtain one 24 hour sample (12:00 to 12:00) one morning rush hour sample (06:00 to 10:00) and one evening rush hour sample (16:00 to 20:00) per day.

In the previous study (Moore 1999 unpublished) the L30 was found to draw between 32 to 34 L min^{-1} and the two L100's were found to draw between 88 to 93 L min^{-1} and 79 to 85 L min^{-1} respectively. Variations were partly due to the loadings on the filters but flow rates were found to be stable to within 3 L min^{-1} during any one sample run by recording flow rates before and after sample runs.

Volumes of air sampled were determined using three dry gas meters in series with the pump and filters. Therefore actual flow rates are not crucial, it was only necessary to ensure a suitable sample volume for accurate analysis. Meter readings, flow rates and filter numbers were logged for each sample station each day.

10.1.2 Monitoring Of PM_{10} With AirMetric Minivol™ Monitors

Two Airmetric MiniVol™ portable monitors were used to monitor PM_{10}. These monitors utilised an impaction pre-seperator to achieve a $_{10}\,\mu m$ AD cut point. The filter housing was incorporated into this unit which was fitted to the monitor via a snap lock fitting.

These monitors operated at a flow rate of 5 L min^{-1} which was guaranteed by an internal flow meter and an integral flow control circuit. A low flow rate results in shut down of the monitor; this was verified as being accurate in a previous study. The monitors were battery powered using large purpose built, rechargeable powerpacks, allowing for sample runs of up to 24 hours. Powerpacks were recharged on site in waterproof boxes, using the transformers supplied. Internal circuits shut down the monitor if the battery was at low power to safeguard the life of the battery.

Internal timers allowed for a range of sample periods to be pre-programmed and an internal time elapsed clock recorded sample time in 100^{th}'s of an hour. Sample times, battery numbers, filter numbers and flow rates were recorded before and after each sample run. Samples were taken for 24 hour (12:00 to 12:00) and rush hours (06:00 to 10:00 and 16:00 to 20:00 on the same filter) periods.

10.1.3 Monitoring With The Partisol 2000 Starnet System

One Partisol 2000 Starnet System was used to monitor PM_{10}, $PM_{2.5}$ and PM_1. This monitor is a USEPA standard method for monitoring PM_{10}, consisting of one hub unit and three satellites and is mains powered. The hub unit contained a pump, switching gear, control circuitry, a filter housing and a pre-separator head of choice. The satellites consisted of a filter housing and pre-separator of choice. The satellites were connected to the hub via 3m of air-line. The control system allowed for versatile user-defined programming of the unit (giving up to eight sample periods, two per station), full control of flow rates, which sample station was in use and logged ambient temperature, pressure, system status, sample dates, time, operating station, total volume sampled and standard volume sampled (relative to 2^0C

and 1 atmosphere), sampling time and valid sampling time on a half hourly basis and a sample run basis. This information was stored in a circular buffer allowing for up to 2 months data (over writing the first data when full) and was retrieved as comma separated variables, using the relevant software via an RS232 link (this can be remote).

The PM_{10} pre-separator used was an impaction system. $PM_{2.5}$ and PM_1 pre-separators were both cyclonic the cut points of all the pre-separators were achieved at 17.6 L min^{-1} (approximately 1 m^3 sample volume $hour^{-1}$). Control circuitry monitored the flow rate and maintained it at ± 5% of this value or considered the volume sampled outside this limit as invalid. The system was programmed to sample for 24-hour periods (12:00 to 12:00) sequencing through all stations on a five-minute basis (Hub, Sat1, Sat2, Sat3, Hub.. etc.).

10.2 Filters And Their Treatment

10.2.1 TSP Monitoring

For the monitoring of TSP; Whatmans GF/A 60mm diameter glass fibre filters were used. These were placed in labelled 90mm diameter, clean, single vent, plastic petri dishes and conditioned for 24 hours in facilities under dust and humidity controlled conditions. The filters were weighed under these conditions on a five figure Ohaus microbalance; humidity, temp, filter ID's and weights were recorded. The balance was calibrated before and after each weighing period (4 hours) (this was found to remain stable during the previous study). Filters were re-weighed after a further 24 hours conditioning and weights were compared, differences over ± 10 μg were considered unacceptable and any such filters were reconditioned and weighed until consecutive weights met the requirements. Any filters that were outside of the tolerances after five weighings were not used. The average of the two consecutive weighings was taken as the clean filter weight.

Filters were never be handled, Whatmans filter tongs were always used. Filters were placed into their labelled petridish and into two re-sealable plastic bags for transportation.

Filters were stored on site in two re-sealable plastic bags and only taken out during sampling. For sampling the filters were placed into the Snap-On housing and exposed as per the sample regime. Filters were changed at 12:00 daily and records kept of which filter was exposed when, filters were immediately replaced in their petridish and two re-sealable bags for storage and transportation back to the lab for analysis.

Filters were conditioned in their petridishes in the clean box facilities for a minimum of 24 hours before weighing as above on the same five-figure balance. Again the average of the two consecutive weighings which met the criteria ($\pm$ 10 μg) was taken as the exposed mass.

10.2.2 PM_x Monitoring Using Partisol And Airmetric Monitors

For the monitoring of all PM_x fractions; Palflex 47 mm diameter, Teflon coated glass fibre filters with integral PNP support were used. Filters were placed in 50 mm labelled, clean, single vent petri dishes in the clean room facilities under temperature, humidity and particulate controlled conditions for a minimum of 24 hours conditioning. Filters were weighed on a Cahn 32, six-figure microbalance. Filter numbers, temperature, humidity and mass was recorded. Repeat weighings were made given a precision of $\pm$ 10 μg the average of the two weighings was taken as the clean mass. Any filters outside the required tolerance were re-weighed until consecutive weighings were made inside the tolerance. Any filters failing to give consecutively precise weighings were not be used. The microbalance was calibrated before weighing and after every ten weighings, if a tolerance of $\pm$ 3.0 μg was exceeded for the zero or calibration weight (200 μg) all ten previous weights were disregarded and filters were re-weighed. If the conditions in the clean room changed by $\pm$ 10% RH or $\pm$ 5^0C weighing was not attempted, or if in progress were stopped and filters weighed during that period re-weighed later.

Filters were never handled and were always manipulated using Whatmans filter tongs. Any filters showing evidence of static charging were neutralised by passing through ionised air, generated using two low-level alpha sources.

Filters for the Partisol were loaded into their labelled filter cases and two re-sealable plastic bags in the clean room. Filters for the Airmetric MiniVols were loaded into their labelled filter housing, which was integral to the pre-separator heads, and two re-sealable plastic bags in the clean room for transportation and on-site storage. Partisol filter holders were loaded into the filter housing for exposure and exposed filters sealed in two re-sealable plastic bags, Airmetric MiniVol heads were fitted to the sampler and heads containing the exposed filters were sealed in two re-sealable plastic bags for transport back to the clean room for analysis.

Filters were replaced into the relevant labelled petri dishes in the clean room facilities, conditioned for a minimum of 24 hours and weighed according to the procedure described above. The average of the two consecutive weighings meeting the tolerance requirements was taken as the loaded mass and recorded.

10.3 Calculation Of Deposited Mass

The samples were conditioned in the clean room for 24 hours and weighed; once before sampling, giving the clean filter mass, and again after sampling giving the loaded filter mass, as outlined above.

The mass of particulate matter collected (M_P) was determined by taking the clean filter mass (FM_C) from the loaded filter mass (FM_L) (equation 1):

$$M_{PM} = FM_L - FM_C \qquad \text{....Equation 1.}$$

This mass was converted to mass per unit volume by dividing M_{PM} by the volume of air that had passed through the filter whilst sampling (V_{STD}) (equation 2):

$$Mass/Vol = \frac{M_{PM}}{V_{STD}} \qquad \text{....Equation 2.}$$

All weights must be reported as μg and volume reported as m^3, the final mass concentrations were reported as μg m^{-3}.

11. RESULTS AND DISCUSSION

In this chapter the raw results (see appendix A) will be presented as summary statistics. although the data collected falls into a log normal distribution statistics have been calculated from the raw data, with the exception of the geometric mean values which were calculated from the logged data (*pers comm* Prof. N. Priest). This has been done as particulate air pollution data is reported as averages (*pers. Comm.* Dr I Williams). It was decided that it was appropriate to report the mean concentration, the geometric mean value, the standard error of the mean and the range (minimum and maximum values). This adequately describes the findings giving information on the average concentration, how 'average' the average is (or the 95% confidence in the mean) and the extremes of the data set respectively.

Each monitor type will be dealt with as a group i.e. the TSP results (24 hour, morning and evening rush hours) obtained using Rotheroe and Mitchell pumps, the results obtained using the Ruprecht and Patashnick Partisol 2000 air sampler (PM_{10}, $PM_{2.5}$ and PM_1) and the results obtained using the Airmetric MiniVol™ (PM_{10} and combined rush hours PM_{10}). This is to enable clear and simple comparisons to be drawn and to allow for a step by step approach to their analysis. The results will then be compared to the results of the summer sample set obtained in the previous study and to the results obtained in the Birmingham study (Harrison *et al* 1997) which included summer/winter comparisons of PM_{10} and $PM_{2.5}$. Finally changes in week day and weekend patterns will be considered

11.1 Partisol Data

100% data capture was achieved over the sampling period; 01/03/99 - 28/03/99 for the Partisol. This provides data which conforms to reference method criteria as designated by the United States Environmental Protection Agency (USEPA) for PM_{10}.

The data collected using the Partisol can be seen in the time series plot (Error! Reference source not found.), data obtained from the two $PM_{2.5}$ stations were averaged and this mean value was plotted for clarity. As all fractions follow extremely similar trends it is safe to assume that they all originate from the same source; in this case the dominant source is traffic (as indicated by the elevated rush hour levels, see section 11.2.1)

Levels of PM_{10} from four Automatic Urban Network (AUN) TEOM monitors were obtained (Netcen/airqual web site 1999) for comparison (see **Figure 16** NOTE: data was averaged over the same 24 hour period as the samples for this study). The NAQS limit for PM_{10} is also plotted to clarify the exceedances recorded at all sites. Levels of $PM_{2.5}$ were obtained from four Automatic Urban Network (AUN) TEOM monitors (Pers. Comm. DETR) for comparison (see **Figure 17** NOTE: data was averaged over the same 24 hour period as the samples for this study). Summary statistics were calculated for all of these sites (PM_{10} and $PM_{2.5}$) and reported as comparison data.

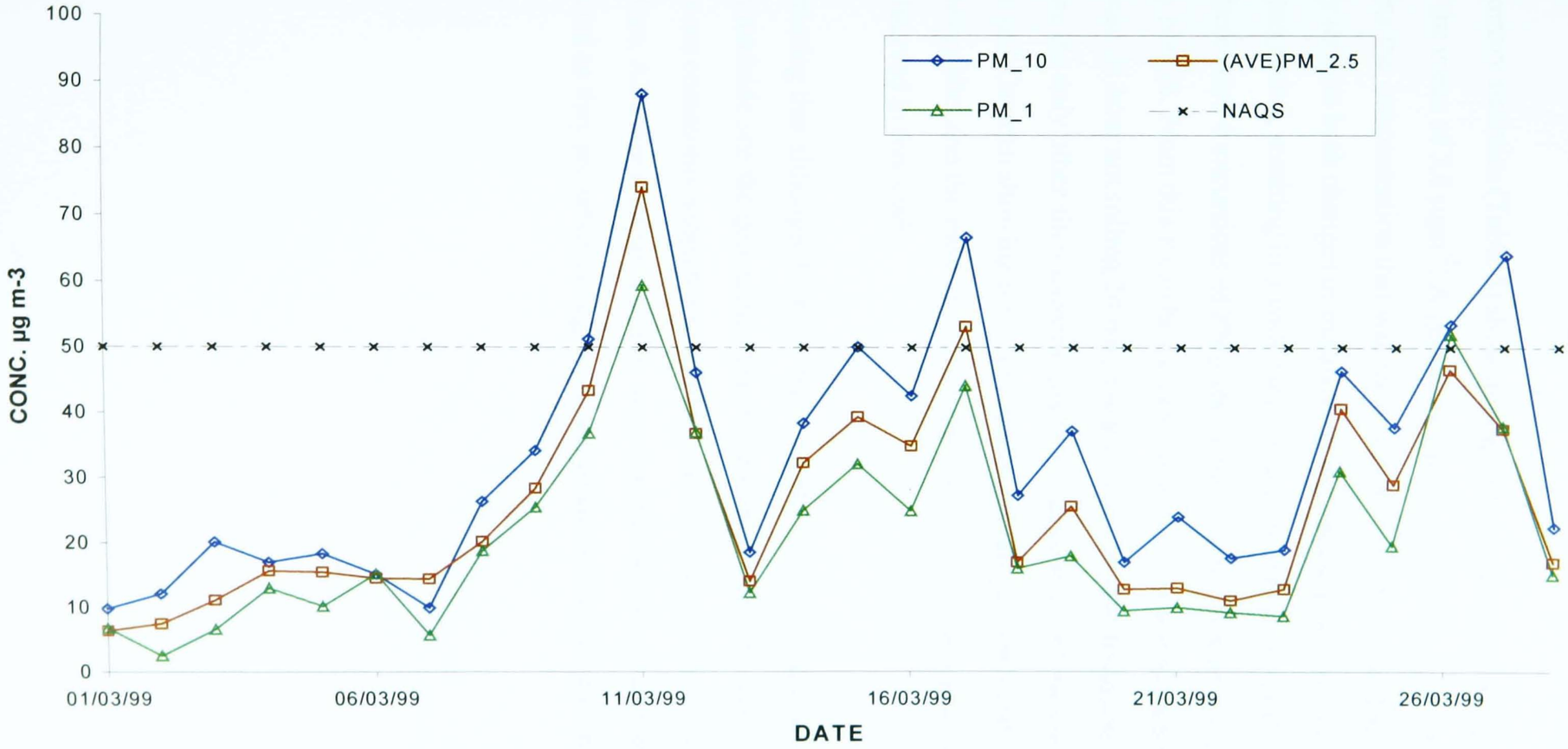


Figure 15 : Time series for all 24-hour Partisol data and NAQS PM_{10} limit, (average $PM_{2.5}$ plotted for clarity)

11.1.1 *Partisol PM_{10}*

The summary statistics (Table 5) show average PM_{10} levels to be 34 μgm^{-3} with a standard error of the mean of 3.8 μgm^{-3}. A geometric mean value of 28 $\mu g\ m^{-3}$ was found, this represents the concentration that was most typical throughout the study. The standard error probably reflects both changes in meteorological conditions and source emission levels over the sample period, resulting in a wide range of concentrations. Over the 28 day sampling period there were 6 excursions of PM_{10} above the running 24 hour mean of 50 $\mu g\ m^{-3}$ limit as set by NAQS. From this it can be expected that the limit was breached (these results being fixed 24 hour not rolling 24 hour means). The Camden Roadside and Bloomsbury sites were the only other sites showing possible excursions, with Bloomsbury showing only one case and Camden showing four. As Camden is both geographically the closest site to the Archway site, and the most similar sitting (roadside) this strengthens confidence in the levels observed in this study.

It is interesting that although Archway has a slightly higher average concentration than Camden roadside site the geometric mean values are almost identical. This suggests that the two sites are commonly subjected to similar levels of PM_{10}, whilst Archway showed higher peak values. All other comparison sites were found to be lower than these two, this would be expected as they are urban background, suburban and background sites respectively.

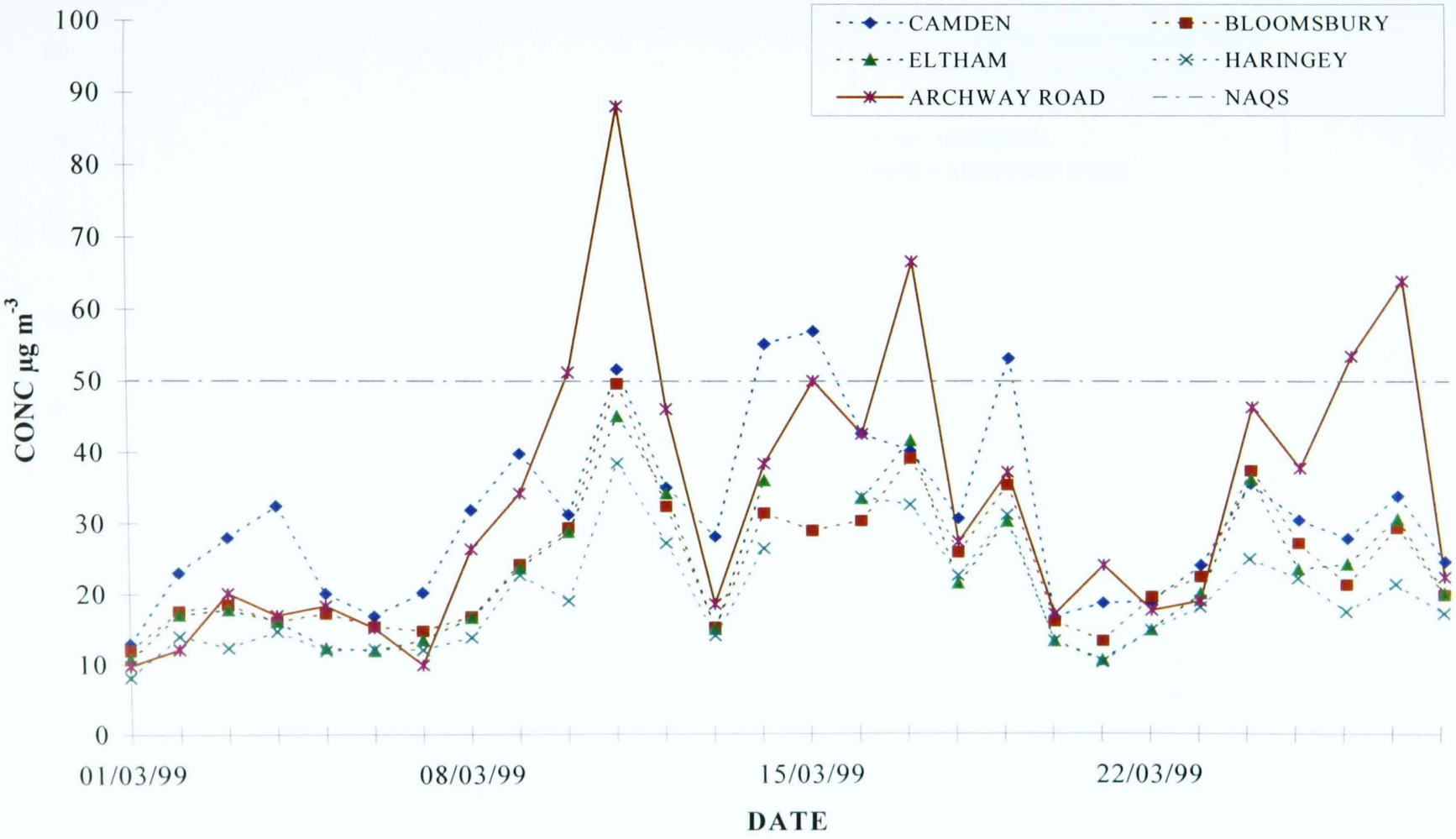


Figure 16 : Time series showing Partisol 24 hour PM_{10}, four AUN comparison sites and NAQS PM_{10} limit

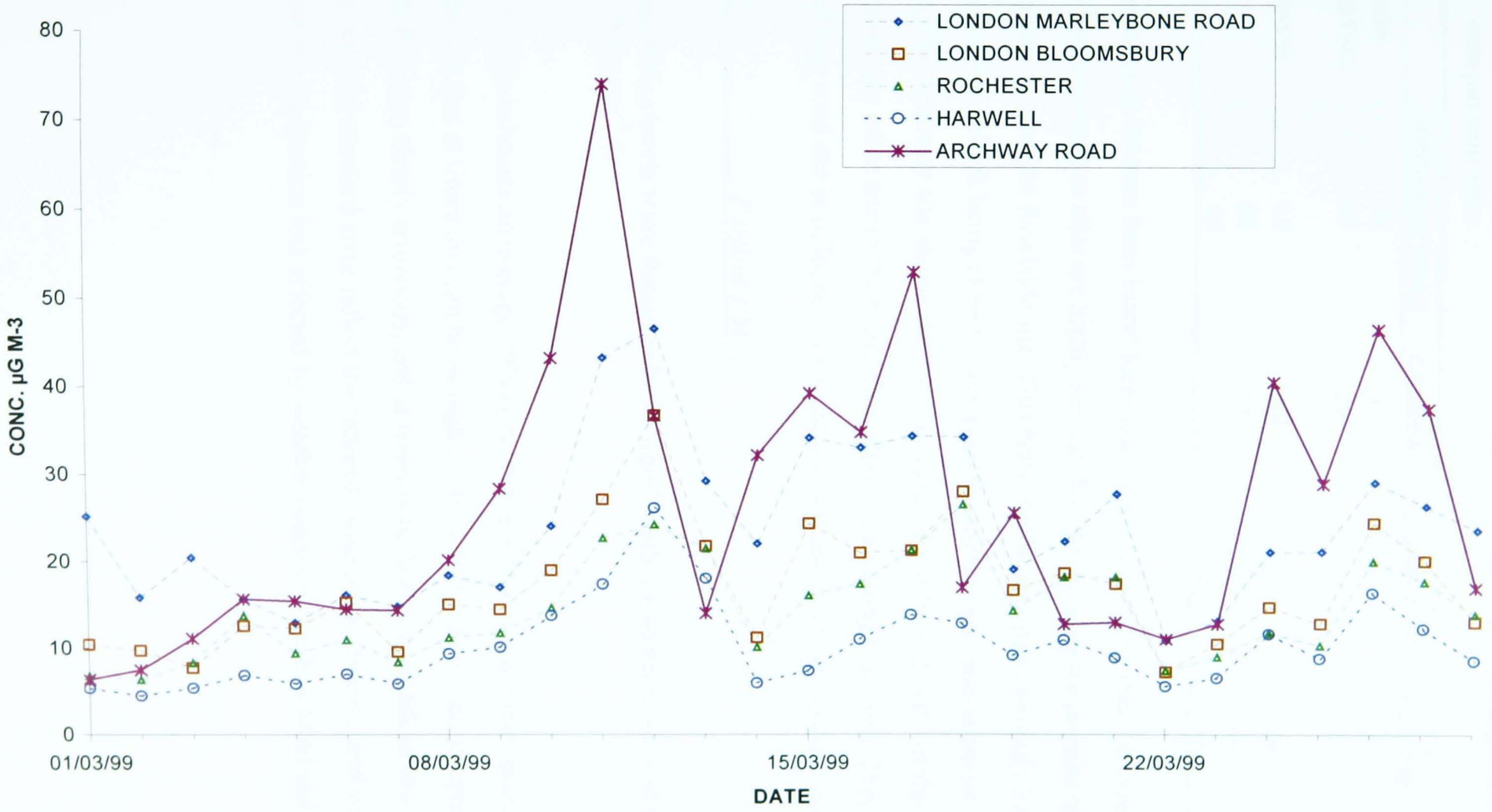


Figure 17: Time series showing Partisol average $PM_{2.5}$ and four AUN comparison sites.

Table 5: PM_{10} Summary statistics for Archway Road PM_{10} (Partisol) and four AUN comparison sites

	ARCHWAY ROAD	CAMDEN	BLOOMSBURY	ELTHAM	HARINGEY
AVERAGE	34	31	24	23	19
GEOMETRIC MEAN	28	29	23	21	18
STDERROR	3.8	2.29	1.74	1.92	1.54
MAX	88	57	50	45	39
MIN	10	13	12	11	8

In general it can be seen from Error! Reference source not found. that the trends displayed by the four comparison sites are highly similar, the site showing the greatest deviation from these trends is Camden Roadside site. This being roadside is more strongly influenced by the traffic flow, which being close to very popular markets and entertainment may be more unique. The Archway site shows the greatest range of results with 54% of the data being higher than any other site (82% higher than all sites excluding Camden). This indicates that the Archway road site is influenced by local sources, and is subject to peak concentrations.

11.1.2 Partisol $PM_{2.5}$

Average $PM_{2.5}$ levels were found to be 26 μgm^{-3} with a standard error of the mean of 3.0 μgm^{-3} (

Table 6). This indicates an average 79% contribution to PM_{10}. The time series plot (Figure 15) indicates that at times this can be as high as 100% PM_{10} (however, samples where $PM_{2.5}$ exceeds PM_{10} are clearly erroneous) and at times contributions can fall as low as 55%. The slightly reduced standard error reflect the reduced range of this fraction and would be expected from a fraction less affected by weather conditions such as wind and precipitation.

Table 6: Showing summary statistics for Archway Road $PM_{2.5}$ and four AUN comparison sites

	ARCHWAY ROAD	MARLEYBONE ROAD	BLOOMSBURY	ROCHESTER	HARWELL
AVERAGE	26	24	17	14	10
GEOMETRIC MEAN	22	23	16	13	9
STDERROR	3.06	1.71	1.31	1.07	0.93
MAX	74	47	37	27	26
MIN	6	11	7	6	4

The comparison data in the time plot (Figure 17) shows similar trends between all sites with the greatest deviations being seen for the Archway Road site. Again it is clear that the Archway site generally had the highest concentrations over this period, (

Table 6) but concentrations also fell below the other sites for 29% of the sample period. This is reflected by the geometric mean values, as for PM_{10} the higher mean becomes almost identical to the Camden site when the data is reworked for the geometric mean value, the typical levels expected at the two sites are very similar, with Archway showing higher peaks. The different trends are considered to be indicative of the effect of differing local sources overlying background concentrations at all sites. Given the apparent level of diversion from the trends displayed at all other sites it could be concluded that the $PM_{2.5}$ at Archway Road is more influenced by local sources (traffic) than the other sites. It must be remembered at this point that comparisons are being made between different monitors and that TEOM's have a reputation for giving low results in the PM_{10} fraction (*Pers. Comm.* Dr B Gorbanuv), which may be enhanced in the finer fractions.

11.1.3 Partisol PM_1

Average PM_1 levels to be 23 μgm^{-3} with a standard deviation of 15 μgm^{-3} giving a standard error of the mean of 2.8 μgm^{-3}. This indicates an average 68% contribution to PM_{10} and an average 85% contribution to $PM_{2.5}$ concentrations. Once again, the greater confidence in the mean indicated by the smaller standard deviation and standard error, are a reflection of

the greater stability (narrower range) of levels of this fraction. Unfortunately there are no sources of comparison data available for this fraction. However, given that $PM_{2.5}$ follows the trends displayed by the other fractions so closely, it can be assumed likely that this fraction would also show elevated concentrations at Archway in comparison to other sites for at least some of the sampling period. It is known that the fine fraction penetrates deeper into the lung, and that sub-micron particles can be more biologically active (COMEAP 1995). This could be extremely relevant with respect to the health implications for people living and working on the Archway road.

11.2 AirMetric™ PM_{10} Data

11.2.1 *24 & Rush-Hour AirMetric™ PM_{10} Data*

Data capture of 93% was achieved for 24 hour PM_{10} using the Airmetric monitor, the two losses were due to a battery failure and one filter which tore on placement in the filter holder (this being impossible to determine until after the sample is taken and the holder is opened). A data capture of 86% was achieved for rush hour PM_{10} using the Airmetric monitor, losses being due to battery failure.

Twenty four hour Airmetric PM_{10} ($^{A}PM_{10}$) data is shown as a time series plot (), plotted with Partisol PM_{10} data ($^{P}PM_{10}$) to show the variations between the two samplers. This variation is evident in the summary statistics, where average $^{A}PM_{10}$ levels were shown to be 38 $\mu g\ m^{-3}$, with a standard deviation of 23 $\mu g\ m^{-3}$, giving a standard error of the mean of 4.5 $\mu g\ m^{-3}$. This indicates an over sample of 4$\mu g\ m^{-3}$ per sample and indicates that, on average, $^{A}PM_{10}$ represents 112% of $^{P}PM_{10}$. The higher range of results resulted in a higher standard deviation and this, combined with the reduced sample set, reduced confidence in the mean value as shown by the higher standard error (in comparison to $^{P}PM_{10}$). This is as would be expected for a cheaper sampler built to less stringent tolerances. It could however be of importance as there would have appeared to have been three further excursions beyond the NAQS limit of 50 $\mu g\ m^{-3}$ if values obtained by this monitor were relied on.

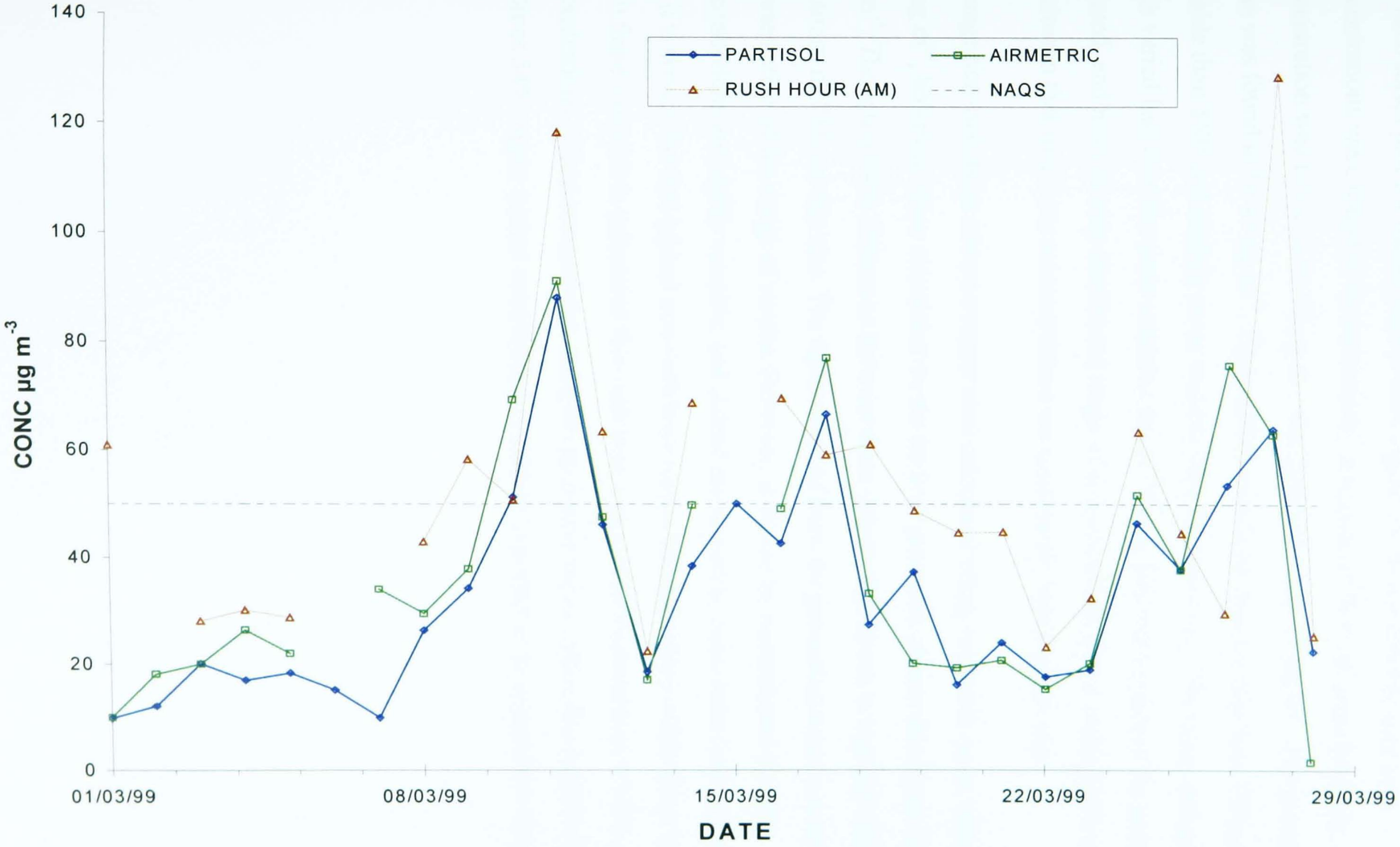


Figure 18 : Time series plot showing Airmetric 24 hour PM10, rush hour PM10, Partisol PM_{10} and NAQS PM_{10} limit.

11.2.2 AirMetric Rush Hour PM_{10} Data

The time series plot for the Airmetric data, Figure 18, shows that the rush hour concentrations were found to be consistently in excess of 24-hour concentrations. The mean concentration was found to be 52 $\mu g\ m^{-3}$, the standard error; 5.5 $\mu g\ m^{-3}$. The geometric mean was found to be 47 $\mu g\ m^{-3}$. These statistics indicate that the rush hour PM_{10} was less variable than TSP and slightly more variable than 24 hour PM_{10}. The mean and geometric mean varied less than the same statistics for 24 $^{A}PM_{10}$, this was a result of the generally elevated, and more evenly distributed range of concentrations found which leads to the conclusion that rush hour concentrations are consistently heavy at this site.

Average non-rush hour concentrations were calculated using Airmetric mean values and a 31 $\mu g\ m^{-3}$, however when calculated on the basis of geometric means this figure falls to 20 $\mu g\ m^{-3}$. There is a 64% difference between these values, this serves to highlight the variations of PM_{10} at this site. The figure derived from the geometric mean is more representative of the range of results. However, it should be remembered that the concentrations are highly variable, and indeed are subject to some error (see section 11.3.1). and it is concluded that typical non-rush hour values lie somewhere within these two values. From these values it is calculated that rush hour concentrations contribute 45.6% of daily concentrations. When recalculated using the geometric mean values this contribution becomes 54%, again typical contributions could be expected to lie somewhere between.

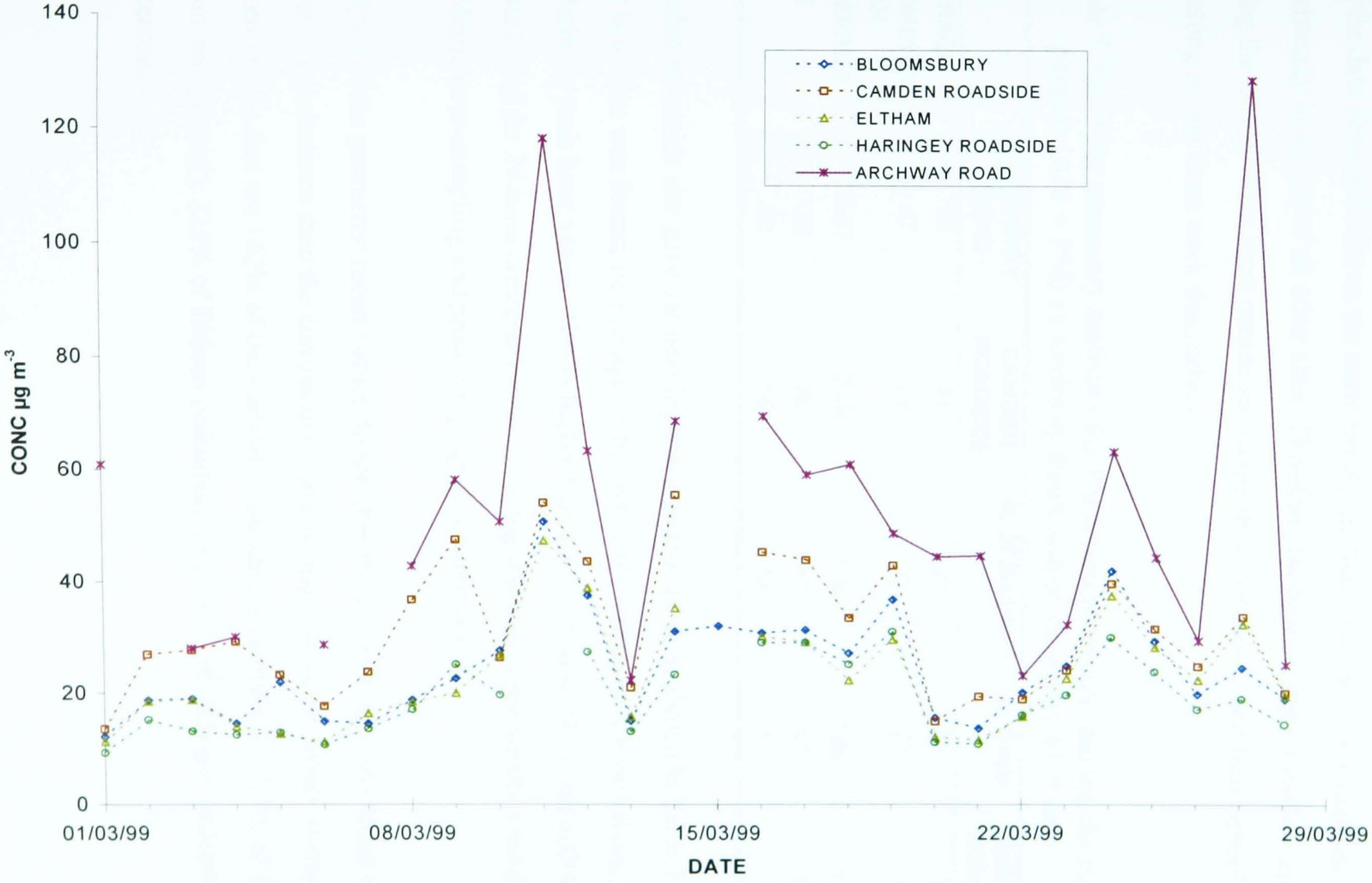


Figure 19 : Time series plot showing the Airmetric rush hour concentrations and comparison AUN sites.

The rush hours were extracted from the PM_{10} data used for Partisol 24 hour comparison and plotted with this rush hour data in the time series plot Figure 19. From this it can be seen that the data obtained follows the same trends and that Archway concentrations were consistently in excess of all other sites. Therefore, the time of highest public exposure is during the period when most people are taking their children to and from school and travelling to and from work themselves.

Table 7: Showing summary statistics for PM_{10} concentrations during the rush hour periods (AM + PM) at Archway Road and comparison AUN sites

	ARCHWAY ROAD	CAMDEN ROADSIDE	BLOOMSBURY	ELTHAM	HARINGEY ROADSIDE
AVERAGE	52	31	25	23	19
GEOMETRIC MEAN	47	29	23	21	18
STDERROR	5.37	2.29	1.80	1.86	1.32
MAX	129	56	51	47	31
MIN	22	14	12	11	9

Camden Roadside site gave the next highest concentrations as shown in Table 7. Archway rush hour data was found, on average, to be 168% of Camden rush hour values, and 274% of Haringey rush hour values. This is higher than the 123% and 200% respective average values found for 24-hour concentrations, clarifying that this is not simply a result of the AirMetric over-sampling and producing higher concentrations.

Analysis of the geometric mean values do not alter the fact that Archway Road is subject to higher concentrations than the comparative sites during rush hours, infact Archway shows concentrations that are 162% of the Camden roadside concentrations, 204% of Bloomsbury (urban background), 223% of Eltham (suburban) and 261% of Haringey (suburban) concentrations.

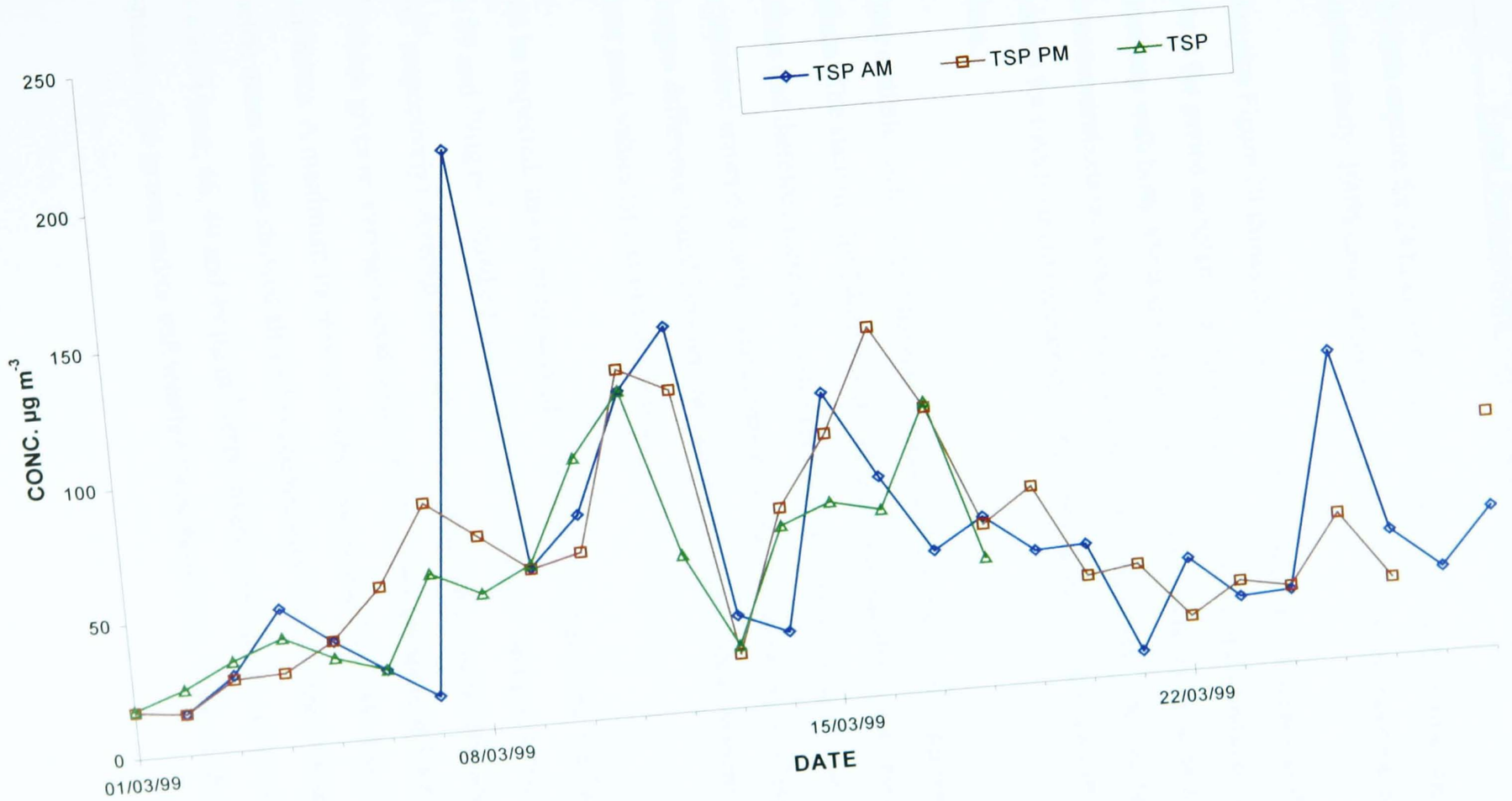


Figure 20 : Time series plot showing the Airmetric rush hour concentrations and comparison AUN sites.

11.3 Total Suspended Particulate (TSP) Results

There was 64% data capture for 24 hour TSP; this was due to the requirement of the L30 monitor for another study. 100% data capture was achieved for both rush hour samplers.

The time series plot Figure 20 shows that 24-hour TSP followed similar trends to Partisol PM_{10} throughout the period sampled. The time series plot indicates the variability of rush hour concentrations with both AM and PM rush hour concentrations found to be higher than 24 hour concentrations on various occasions and lower on others. There is, however, a general tendency for rush hour concentrations to be either equal to or in excess of 24-hour concentrations.

The summary statistics indicate that the above observation is true for evening rush hour concentrations. The statistics for 24-hour TSP indicate more variability than for the various PM_X fractions and therefore there is less confidence in the mean (58 $\mu g\ m^{-3}$) as indicated by the larger standard errors 6.8 μgm^{-3}. The geometric mean was found to be 49 $\mu g\ m^{-3}$. This was the largest difference found between the two statistics for 24-hour samples, reflecting the extreme peak values typical of this fraction.

As would be expected, this is more marked in the case of AM and PM rush hour samples (means: 59 and 79$\mu g\ m^{-3}$, standard errors: 8.7 and 15.3 $\mu g\ m^{-3}$ and geometric means: 46 and 59 $\mu g\ m^{-3}$ respectively). Average non-rush hour concentrations were calculated to be 53.5 $\mu g\ m^{-3}$, which gives an average elevation of 10% for AM rush hours and 40% elevation for PM rush hours. A maximum increase of 400% was recorded for TSP AM on 08 March. Geometric mean values showed all TSP concentrations to be similar (AM and PM rush hours and 24 hour; 46, 49 and 49 $\mu g\ m^{-3}$ respectively), this can be explained by the lack of resuspension due to wet and/or still weather throughout much of this study.

11.3.1 Field Blanks (Associated errors)

Procedural blanks, which followed the entire sampling and analytical protocol, were taken into the field to estimate errors associated with the handling and transport of filters. Table 8 shows the summary statistics generated from the results of their weight changes.

Table 8: Summary statistics for field blanks

STATISTIC	TSP	AIRMETRIC	PARTISOL
AVERAGE	-4	9	4
STDEV	13	6	3
STDERROR	4.1	2	0.9
MAX	15	16	11
MIN	-30	-3	0
ALL RESULTS IN $\mu g\ m^{-3}$			

The TSP filters (Whatmans GFA 60 mm glass fibre) were found to be prone to both weight gains and losses of substantial mass. The average was for a loss of 4 μg, but as the standard error indicates this was highly variable. Weight losses as large as 30 μg and as a gain of 15 μg were recorded. The reasons being a combination of fibre loss from the fragile filters and the lack of a filter holder during transit (allowing for more contamination). It would have been preferable for weight change to be less erratic, but as this was the fraction for which the largest samples were collected and therefore the influence of filter weight change was the lowest, such variation can be accepted.

The results found for the AirMetric were similar to the summer study (where an average 8 μg loss was recorded). The average of 9 μg weight loss found in this study could be significant but it is evident that this is not a constant error, the standard error of the mean shows the variation to be considerable and the max. observation of a 16 μg gain and the min of a loss of 3 μg show this to be the case. Loss was due to the loss of individual fibres that comprise the PNP support backing of the filter, gains were due to deposition of mass from the filter holder. Both of the previous problems are attributable to the holder design, a screw fitting housing, once the filters are housed it is impossible to determine their condition.

Partisol filters showed a very favourable average gain of 4 μg. The standard error was low 0.9 and reflects reasonable confidence in the mean. The maximum observation was 11 μg which was mainly the result of one isolated gain (which remains unexplained). This serves to reinforce the requirements of following a stringent protocol.

The average 9 μg weight gain for AirMetric filters compared to the average 4 μg weight gain for Partisol filters must be viewed in terms of their impact on the final mass concentrations found. The Partisol filter weight gain represents a 0.7 μg m^{-3} error for 24 hour PM_{10} samples, the AirMetric error represents 1.25 μg m^{-3} for 24 hour samples and a 3.75 μg m^{-3} error for rush hour samples. This could be seen as a 2% error for the Partisol PM_{10}, a 2.8% error for $PM_{2.5}$ and a 3% error for PM_1 (for this particular sampling regime) and a 3.7% error for 24 hour AirMetric and a 7.2% error for the rush hour samples.

Although these errors are acknowledged here, the data in this study has not been corrected. This is because such data manipulation would alter the relationships found between the two PM_{10} monitors and it is the author's intention to compare these monitors directly. A second reason is because the data obtained from the summer sampling regime was in its untreated form and therefore correction of this data set would alter summer/winter ratios.

11.4 Regression Relationships

Regression relationships were calculated for all possible fraction combinations (see Appendix B.1 for all regression plots). This was in order to identify any possible trends, to clarify where no trends exist and also to facilitate summer/ winter comparisons. A complete set of regression relationships and their correlation coefficients were calculated for the summer sampling period as reported in section 11.6.

11.4.1 $PM_{2.5}$ V $PM_{2.5}$ (the reliability of Partisol data)

It was considered that analysis of the two 24 hour $PM_{2.5}$ samples obtained daily using the Partisol (using two of the three satellites: Sat 1 and Sat 2) would give an indication of the reproducibility of Partisol data. A relationship of:

$PM_{2.5}$ (sat 1) = 1.0 $PM_{2.5}$ (Sat 2) + 0.0

with an R^2 value of 1.0 would represent a perfect scenario. A relationship of:

$PM_{2.5}$ (Sat 1) = 0.9537(Sat 2) + 0.4782

with an R^2 value of 0.9822 was found which gives an average error of 0.5 μg per sample. The R^2 value and regression equation indicates that the two satellites sampled the same fraction with a high degree of accuracy.

11.4.2 Partisol PM_{10} V Airmetric PM_{10} (The reliability of the Airmetric monitor)

Given that the Partisol is a USEPA reference method it was considered that the correlation of this monitor and the AirMetric monitor would indicate the latter's suitability as a PM_{10} monitor. Again the expectancy is of a one to one relationship:

AirMetric PM_{10} = Partisol PM_{10} + 0.0

the actual relationship found was:

AirMetric PM_{10} = 1.0999 Partisol PM_{10} + 0.2679

with an R2 of 0.8977. This indicates an average error of +10% of the Partisol value and an additional systematic error of 0.3 μg, the R^2 value indicating a high degree of correlation between the two. The 11% error calculated here compares well to the 12% error calculated from the 24-hour means. This suggests that treated with care, the AirMetric monitor is a reliable monitor for PM_{10}.

11.4.3 PM_{10}, $PM_{2.5}$ and PM_1 Relationships

Regression analysis for the three fractions monitored by the Partisol can be seen in Table 5. The R^2 values reflect the fractions being compared, that is to say the strongest relationship was found for PM_{10} V $PM_{2.5}$, with the $PM_{2.5}$ V PM_1 relationship being almost as strong. The PM_{10} V PM_1 relationship was the weakest, but with an R^2 value of 0.903 this still represents a very close relationship between the two fractions.

Table 9: The regression equations and their R^2 values for all Partisol monitored fractions for winter sample period (01/03/99 - 28/03/99)

FRACTIONS	REGRESSION EQUATION	R^2 VALUE
PM_{10} Vs $PM_{2.5}$	$PM_{2.5}$ = 0.8037 PM_{10} - O.833	0.943
PM_{10} Vs PM_1	PM_1 = 0.7202 PM_{10} - 2.401	0.9034
$PM_{2.5}$ Vs PM_1	PM_1 = 0.8837 $PM_{2.5}$ -1.3347	0.9318

All values are in μg m-3

The regression equations suggest that $PM_{2.5}$ represents 80% of PM_{10}, minus roughly one microgram, which represents 3% of the mean. Therefore this analysis suggests that on average $PM_{2.5}$ contributes 77% to PM_{10}.This compares well with Harrison *et al* (1997) who, during the study in Manchester, found the relationship:

$$\mathbf{PM_{2.5} = 0.83\ PM_{10}\ 0.92}\ (R^2 = 0.93)$$

It was found that PM_1 was making a 72% minus 2.4 μg m^{-3} (7% of mean), averaging as a 65% contribution to PM_{10}. An 88% contribution minus 1.3 μg m^{-3} (5% of mean $PM_{2.5}$) was found, giving an average contribution of 83% contribution to $PM_{2.5}$. These contributions compare well with the percentage contributions estimated using mean values; 77%, 65% and 83% respectively. The relationships above are in the order that would be expected given the knowledge of how these fractions fit into the mass versus AD for typical urban aerosols. The point of interest is the high degree of correlation found for all combinations, this implies that a local traffic source dominates the Archway aerosol.

It should be remembered that this study took place over a relatively short period of time, and that a larger data set may have highlighted variations from the patterns observed in this study. One aspect of interest was the range of weather conditions during the sampling period; from exceptionally warm for the time of year ($30^{O}C$) to near zero temperatures, from heavy rain to three consecutively clear days and a range of wind conditions were also noted. These changes in conditions will have contributed to the range of results obtained, therefore it may be that this data set is not truly representative of a typical winter data set. A longer sampling regime would reduce the influences of such variable weather on the final statistics and result in increased confidence in the means.

11.5 All Other Correlations

Regression relationships and their R^2 values were calculated for all other possible combinations of fractions see Table 10. A comparison of the AirMetric PM_{10} correlation's and their respective Partisol PM_{10} correlation's will help to clarify the performance of the AirMetric monitor.

The relationships between AirMetric PM_{10} ($^{A}PM_{10}$) and Partisol $PM_{2.5}$ and PM_1 ($^{P}PM_{2.5}$ and $^{P}PM_1$) were weaker than those found for the Partisol, with respective R^2 values of 0.91 and 0.68. This may be the result of different sampler designs and therefore, a difference in the actual fraction being monitored. However the 3.7% error for the $^{A}PM_{10}$ field blanks accounts for some of this discrepancy, reducing the apparent influence of oversample on the $^{A}PM_{10}$ concentrations.

When the 24 hour TSP (TSP_{24}) correlation's with $^{A}PM_{10}$ and $^{P}PM_{10}$ are examined it appears that $^{A}PM_{10}$ is more associated with TSP concentrations, $^{A}PM_{10}$ contributing 76% and $^{P}PM_{10}$ contributing 66% to TSP concentrations. This may be due to the AirMetric sampling more of the TSP than the Partisol. When the evidence of weight gain in the field blanks are considered, it would appear that the above assumption is wrong. This may well account for much of the difference observed.

Evidence that the $^{A}PM_{10}$ was over sampling comes from the fact that $^{A}PM_{10}$ is biased towards TSP. The $^{A}PM_{10}$ was more strongly associated with TSP (R^2 = 0.976, $^{P}PM_{10}$ R^2= 0.852) and more weakly associated with PM_1 (R^2 = 0.679, $^{P}PM_{10}$ R^2= 0.903). If the elevated $^{A}PM_{10}$ values were a result of the filter weight gains then this would not be expected. It should be concluded that the final $^{A}PM_{10}$ values were influenced by these factors.

Table 10: All other regression equations and their R^2 value for winter sample period (01/03/99 - 28/03/99)

FRACTIONS	REGRESSION EQUATION	R^2 VALUE
$^{A}PM_{10}$ Vs $^{P}PM_{2.5}$	$^{P}PM_{2.5}$ = 0.7147 $^{A}PM_{10}$ - 1.4588	0.907
$^{A}PM_{10}$ Vs $^{P}PM_{1}$	$^{P}PM_{1}$ = 0.8404 $^{A}PM_{10}$ - 6.7599	0.6792
TSP_{24} V $^{P}PM_{10}$	$^{P}PM_{10}$ = 0.6638 TSP_{24} - 4.3036	0.8519
TSP_{24} V $^{A}PM_{10}$	$^{A}PM_{10}$ = 0.7551 TSP_{24} - 3.433	0.9761
TSP_{24} V $^{P}PM_{2.5}$	$^{P}PM_{2.5}$ = 0.5672 TSP_{24} - 5.19	0.8934
TSP_{24} V $^{P}PM_{1}$	$^{P}PM_{1}$ = 0.4614 TSP_{24} - 4.0701	0.8106
TSP_{AM} V TSP_{PM}	TSP_{PM} = 0.3885 TSP_{AM} + 37.664	0.2679
TSP_{PM} V TSP_{24}	TSP_{24} = 0.5838 TSP_{PM} + 17	0.5852
TSP_{AM} V TSP_{24}	TSP_{AM} = 0.1917 TSP_{24} + 45.226	0.1229
All values in µg m-3	**^{A} = AirMetric ^{P} = Partisol**	

One unexpected observation is the high degree of correlation between the TSP_{24} and $PM_{2.5}$ and PM_1 (R^2= 0.8934 and 0.8106 respectively). This would suggest the same source of all particulates at the site. It is possible that the suppression of deposited particulates due to wet weather throughout this study has had an influence on these results, which would be expected to elevate TSP more than $PM_{2.5}$ (Harrison *et al* 1998). This was found to be the case in the summer study (see TSP_{24} correlations in Table 12). The weather was very mixed over the sampling period (as previously mentioned), and therefore suppression of TSP cannot be explained by wet conditions. It may be that, precipitation and runoff in the preceding weeks or months had removed deposited particulate, reducing the amount available for later resuspension. A more detailed analysis of long term data or analysis of street dust levels would be required to clarify this.

As expected, there are no clear relationships between 24-hour TSP and rush hour TSP concentrations or for rush hour PM_{10} and 24 hour PM_{10}. This simply reflects the fact that rush hour traffic densities do not influence traffic patterns throughout the day, any weak trends would be obscured by the influence of random weather conditions.

11.6 Comparison of summer and winter regression analysis

All correlations showed stronger relationships during winter than summer (see Table 12 and Table 13), with the one exception of $^{A}PM_{10}$ V's $^{P}PM_{1}$. This was by far the weakest correlation found for winter data, which is possibly due in part to erroneous data, other than this it remains unexplained. The increased R^2 values for $^{P}PM_{1}$ V's $^{A}PM_{10}$ and for $^{P}PM_{2.5}$ V's $^{P}PM_{2.5}$ indicate a higher degree of accuracy with respect to procedure throughout this study, this will be reflected in the other results.

The better correlations found for all PM_X data during the winter probably reflect the domination of one source (traffic) and the suppression of the wind blown resuspension. Resuspended dust can influence PM_{10} and $PM_{2.5}$ to a much lesser degree, as reported by Harrison *et al* (1997) and QUARG (1995). This assumption appears to be strengthened by the fact that the least strengthened relationship of these three is that of $^{P}PM_{2.5}$ V $^{P}PM_{1}$.

The change in the percentage mass one fraction contributes to another (i.e. $PM_{2.5}$ to PM_{10}) was estimated from both regression equations and mean values (all data). The results were found to be relatively similar (Table 11). In each case the discrepancy between the two methods is in the region of 0.5 $\mu g\ m^{-3}$, this is well below limits of detection for this study and therefore could be considered to be the same. Analysis of collocated TEOM $PM_{2.5}$ and PM_{10} monitors could reveal more detailed patterns as their data resolution and limits of detection are far superior.

Table 11: Showing the increased contribution of one fraction to another in the winter study, both estimation from the regression equations and the mean values are shown

FRACTION CONTRIBUTION	REGRESSION ESTIMATE	MEAN ESTIMATE
$PM_{2.5}$ to PM_{10}	4.4%	3.2%
PM_1 to PM_{10}	4.7%	5.7%
PM_1 to $PM_{2.5}$	2.4%	3.9%

Table 12: Regression relationships between the fractions monitored at Archway Road for summer 1998

FRACTIONS	REGRESSION EQUATION	R^2 VALUE
$^{P}PM_{10}$ Vs $^{A}PM_{10}$	$^{P}PM_{10} = 1.034\ ^{A}PM_{10} + 1.944$	0.79
$^{(1)}PM_{2.5}$ Vs $^{(2)}PM_{2.5}$	$^{(2)}PM_{2.5} = 1.042\ ^{(1)}PM_{2.5} - 0.715$	0.857
$^{P}PM_{10}$ Vs $^{P}PM_{2.5}$	$PM_{2.5} = 0.76\ PM_{10} - 0.294$	0.823
$^{P}PM_{10}$ Vs $^{P}PM_{1}$	$PM_{1} = 0.673\ PM_{10} - 0.773$	0.755
$^{P}PM_{2.5}$ Vs $^{P}PM_{1}$	$PM_{1} = 0.859\ PM_{2.5} - 0.169$	0.873
$^{A}PM_{10}$ Vs $^{P}PM_{2.5}$	NOT REPORTED	0.819
$^{A}PM_{10}$ Vs $^{P}PM_{1}$	NOT REPORTED	0.775
TSP Vs $^{P}PM_{10}$	NOT REPORTED	0.047
TSP Vs $^{P}PM_{2.5}$	NOT REPORTED	0.065
TSP Vs $^{P}PM_{1}$	NOT REPORTED	0.106
TSP Vs $^{A}PM_{10}$	NOT REPORTED	0.05

All values in µg m-3 **^{A} = Airmetric ^{P} = Partisol**

Table 13: All regression equations and their R2 value for winter sample period (01/03/99 - 28/03/99)

FRACTIONS	REGRESSION EQUATION	R2 VALUE
$^{P}PM_{10}$ Vs $^{A}PM_{10}$	$^{A}M_{10} = 1.0999\ ^{P}PM_{10} + 0.2679$	0.8977
$^{(1)}PM_{2.5}$ Vs $^{(2)}PM_{2.5}$	$^{(1)}PM_{2.5} = 0.9537^{(2)}PM_{2.5} + 0.4782$	0.9822
$^{P}PM_{10}$ Vs $^{P}PM_{2.5}$	$PM_{2.5} = 0.8037\ PM_{10} - 0.833$	0.943
$^{P}PM_{10}$ Vs $^{P}PM_{1}$	$PM_{1} = 0.7202\ PM_{10} - 2.401$	0.9034
$^{P}PM_{2.5}$ Vs $^{P}PM_{1}$	$PM_{1} = 0.8837\ PM_{2.5} - 1.3347$	0.9318
$^{A}PM_{10}$ Vs $^{P}PM_{2.5}$	$^{P}PM_{2.5} = 0.7147\ ^{A}PM_{10} - 1.4588$	0.907
$^{A}PM_{10}$ Vs $^{P}PM_{1}$	$^{P}PM_{1} = 0.8404\ ^{A}PM_{10} - 6.7599$	0.6792
TSP_{24} V $^{P}PM_{10}$	$^{P}PM_{10} = 0.6638\ TSP_{24} - 4.3036$	0.8519
TSP_{24} V $^{A}PM_{10}$	$^{A}PM_{10} = 0.7551\ TSP_{24} - 3.433$	0.9761
TSP_{24} V $^{P}PM_{2.5}$	$^{A}PM_{2.5} = 0.5672\ TSP_{24} - 5.19$	0.8934
TSP_{24} V $^{P}PM_{1}$	$^{A}PM_{1} = 0.4614\ TSP_{24} - 4.0701$	0.8106

All values in µg m-3 **A = Airmetric P = Partisol**

11.7 Week Day and week end trends (summer and winter data sets)

Summary statistics were calculated for both the winter and summer data sets (see Table 14 and Table 15 respectively). Winter concentrations were found to be consistently higher for all fractions during all periods analysed, with the exception of weekend morning rush hour TSP. As this study only sampled four-week end periods, this may be a result of non-typical conditions, further study would be required to clarify this anomaly. However it is clear that winter concentrations are consistently in excess of summer, this is in keeping with the findings of Harrison *et al* (1997) and QUARG (1995).

Table 14: Summary statistics for all data, week days and week ends (winter data set 01/03/1999 - 28/03/1999)

		OPEN FACED			PARTISOL 2000			AIRMETRIC MINI-VOL	
DATA SET	STATISTIC	TSP_{AM}	TSP_{PM}	TSP	PM_{10}	(AVE)$PM_{2.5}$	PM_1	A PM_{10}	A PM_{10} (RH)
ALL DATA	N	28	28	18	28	28	28	26	24
	MEAN	59	61	58	34	27	23	38	52
	GEOMETRIC MEAN	46	49	49	28	21	17	29	47
	STD ERROR	8.7	6.6	6.8	3.8	3	2.8	4.5	5.5
	MAX	214	137	121	88	74	59	91	129
	MIN	8	15	23	10	7	3	2	22
WEEK DAYS	N	20	20	14	20	20	20	19	18
	MEAN	72	60	60	36	28	24	40	51
	GEOMETRIC MEAN	58	49	52	31	23	18	33	47
	STD ERROR	11.2	7.4	7.5	4.7	3.6	3.4	5.3	7.5
	MAX	214	137	121	88	74	59	91	129
	MIN	15	20	23	10	10	6	2	22
SAT SUN	N	8	8	4	8	8	8	7	6
	MEAN	30	58	44	25	19	18	29	56
	GEOMETRIC MEAN	26	52	39	21	17	16	20	46
	STD ERROR	5.7	9.2	11	6.4	3.5	3.5	7.9	15.9
	MAX	53	88	66	64	38	38	63	129
	MIN	8	20	23	10	10	6	2	22

All values in μg m-3

Table 15: Summary statistics for all data, week days and week ends (summer data set 29/06/1998 - 10/08/1998)

DATA SET	STATISTIC	OPEN FACED			PARTISOL 2000			AIRMETRIC MINI-VOL	
		TSP_{AM}	TSP_{PM}	TSP	PM_{10}	$(AVE)PM_{2.5}$	PM_1	$A\ PM_{10}$	$A\ PM_{10}$ (RH)
ALL DATA	N	40	42	37	34	33	34	42	17
	MEAN	35	45	23	21	16	13	24	29
	GEOMETRIC MEAN	19	32	41	20	15	13	23	29
	STD ERROR	2.8	3.2	2.4	1.0	0.9	0.7	1.1	1.2
	MAX	111	125	73	36	26	21	51	34
	MIN	15	11	8	11	7	4	13	21
WEEK DAYS	N	29	30	28	25	24	25	30	14
	MEAN	33	47	22	21	16	13	24	29
	GEOMETRIC MEAN	18	32	42	20	15	13	23	28
	STD ERROR	1.9	4.0	2.5	0.8	0.8	0.8	1.3	1.3
	MAX	61	125	47	31	26	21	51	34
	MIN	20	11	8	14	9	6	14	21
SAT SUN	N	12	11	9	10	9	9	12	4
	MEAN	42	39	27	21	15	14	24	30
	GEOMETRIC MEAN	22	31	37	19	14	12	23	30
	STD ERROR	7.5	4.5	6.3	2.5	2.0	1.7	2.3	2.5
	MAX	111	67	73	36	24	21	40	34
	MIN	15	21	10	11	7	4	13	23

All values in µg m-3

Summer/ winter (S/W) ratios were calculated for all fractions (see Table 16). This shows that 24 hour TSP is the fraction showing the greatest increase in winter (summer concentration is 40% of winter concentration). It is interesting to note that the finer fractions are the least stable; PM_1 shows a lower S/W ratio than $PM_{2.5}$ which in turn is smaller than PM_{10} over all time periods. This indicates that levels of TSP increase in the winter, whilst PM_{10} increases less dramatically than levels of $PM_{2.5}$ and PM_1. This will be relevant to health as it is known that the fine and ultra fine fractions are deposited deeper in the lung and sub-micron particulates are more biologically active (COMEAP 1995).

Table 16: Summer/winter ratios for Archway Road

DATA SET	OPEN FACED			PARTISOL 2000			AIRMETRIC MINI-VOL	
	TSP_{AM}	TSP_{PM}	TSP	PM_{10}	$(AVE)PM_{2.5}$	PM_1	A PM_{10}	A PM_{10} (RH)
ALL DATA	0.59	0.73	0.40	0.61	0.59	0.56	0.63	0.55
WEEK DAYS	0.45	0.78	0.37	0.58	0.57	0.54	0.60	0.56
WEEK ENDS	1.40	0.67	0.61	0.84	0.78	0.77	0.82	0.53

Rush hour PM_{10} levels increased more than 24-hour concentrations during the winter study, this may be due to a larger number of people travelling to work during the poor weather of winter, but is most likely to be due to the influence of cold starts. This phenomenon is clarified by the significantly greater increase in AM rush hour TSP concentrations compared to PM rush hour TSP when engine temperatures would be warmer. This pattern may not be as clear throughout the winter as daytime temperatures were relatively high during March 1999. This may be further suppressed in dry and windy weather conditions due to resuspension of road dusts.

All weekday PM_X fractions showed a greater degree of elevation during the winter weekdays than weekends. The mean concentrations indicated that summer concentrations were stable for both weekdays and weekends during summer. Winter patterns were of elevated concentrations during of PM_1 and rush hour PM_{10} during the week end periods and decreased 24 hour PM_{10} and $PM_{2.5}$ concentrations. This can be explained if there were lower traffic densities at week ends during winter with relatively intense concentrations of traffic during rush hours, the elevated rush hour PM_{10} concentrations may result in higher PM_1 concentrations due to a slower deposition rate for fine particulates.

11.8 On the Importance of Geometric means for the Analysis of Environmental Data

There are several methods for estimating the average value of a data set, or it's 'central tendency', each being representative of a particular situation. The problem lies in the way the data set affects the calculated central tendency and the subsequent interpretation of the values obtained. It is important to use the measure that represents the data set, otherwise the danger is of misrepresenting the situation being described.

In the case of this study the data is log-normally distributed, this requires the use of the geometric mean as a measure of average values. The geometric mean is more representative of the data set, as it is not affected by the peak values as strongly as the arithmetic mean. It is calculated by taking the antilog of the average value determined from a log-transformed, positively skewed data set (Elliot J M 1977, Owen and Jones 1977). The positive skew of the data set in this study is the result of typically high peaks in concentration, i.e. most of the data set falls into a lower range of values and a few values are relatively high. The effect of these high values on the mean is to 'pull' it to the right, i.e. a high value which doesn't represent the main body of the data set is reported. The further the skew, or the higher the number of larger values are, the more exaggerated the mean becomes.

It is interesting to note how this analysis, using geometric mean values, has changed the interpretation of the results. The comparisons with AUN sites in particular, resulted in the Archway road site seeming more in keeping with the central London and roadside sites. It is notable however, that when the time series plots and ranges were analysed the Archway site displayed several peak values in excess of the comparison sites. This highlighted the fact that no one statistical value can be used to characterise an environmental data stet, in fact it would appear that a rigorous analysis using all the statistical and graphical tools available to the scientist is required. This can in some ways complicate the issue and make conclusions more difficult to draw, but in the long run provides a fuller picture.

12. CONCLUSIONS

- Mean 24-hour PM_{10} concentrations were found to average 34 $\mu g\ m^{-3}$. This was seen to exceed 50 $\mu g\ m^{-3}$ on six occasions, (using the Partisol data, a USEPA reference method). It is likely that the NAQS limit of 50 $\mu g\ m^{-3}$ as a rolling 24-hour mean was exceeded around these periods.

- Winter PM_{10} concentrations at Archway were found to follow similar tends as AUN sites Camden Roadside, Bloomsbury, Eltham and Haringey. On comparison with these sites, Archway Road mean PM_{10} concentrations were found to be higher for 54% of the sampling period, and if Camden was discluded this increased to 82%. Geometric mean concentrations indicate that overall, the Archway Road site is comparable to the Camden roadside site, despite the presence of many periods of excessive concentrations.

- Mean 24-hour $PM_{2.5}$ concentrations were found to average 26 $\mu g\ m^{-3}$. This was found to be in excess of all AUN comparison sites; Marleybone Road, Bloomsbury, Rochester, and Harwell. With Archway mean $PM_{2.5}$ being 108% of the highest comparison site (Marleybone Road, London central site) and 260% of the lowest comparison site (Harwell, background site). Again the analysis of geometric mean concentrations bring the Archway site in line with the site subject to the next highest mean value, in this case Bloomsbury. Again the Archway Road site shows several occasions where concentrations are in excess of all other sites despite the similarity of geometric means.

- Mean 24-hour concentrations of PM_1 were found to average 23 $\mu g\ m^{-3}$. The geometric mean value was found to be 17 $\mu g\ m^{-3}$, this discrepancy between the mean and geometric mean being due to the strong effect of peak values (a result of local source variations) on the log normally distributed data set. Unfortunately no comparison sites were available.

- $PM_{2.5}$ was found to contribute 79% to PM_{10} during the winter study, PM_1 was found to contribute 68% to PM_{10} and 85% to $PM_{2.5}$ (based on mean values). These were found to be slightly higher than the contributions found during the summer study, which were 76%, 62% and 81% respectively. Regression analysis found similar increases in contributions during the winter study.

- The AirMetric MiniVol™ was found to be a robust and adequate monitor for PM_{10}. However, this monitor was found to oversample; on average PM_{10} found using this equipment was112% in comparison to the Partisol during this winter study (110% in the previous summer study). Interestingly, comparison of geometric mean values obscures this and only indicates a 4% error,(which could apparently be explained by the field blank weight gains). The conclusion is that there is some systematic oversample which is occasionally increased by extreme weight gain of filters (which the geometric mean obscures).

- Analysis of field blanks attributes some of this oversample, on average 9 μg (on average 3.7% for 24 hour samples and 7.2% for 8 hour rush hour samples), to filter weight gain during the whole sampling procedure. Field blank errors for the Partisol were found to be, on average 4 μg (on average 2% for PM_{10}, 2.8% for $PM_{2.5}$ and 3% for PM_1), based on the Partisol's programme cycle for this study.

- Rush hour $^{A}PM_{10}$ concentrations were found to be 123% of 24-hour $^{A}PM_{10}$ during the winter study (based on mean values). This compared well with the 121% value found during the summer study. PM_{10} comparison sites all showed lower rush hour values, Archway levels being between 168% of the Camden roadside concentrations and 247% of Haringey concentrations. This effect was not removed on analysis using geometric means. Therefore, rush hour concentrations contribute 45.6% of daily concentrations, using the geometric mean values this contribution becomes 54%, it is concluded that the level of rush hour contribution will typically vary between these two values.

- Mean 24 hour TSP was found to be 58 $\mu g\ m^{-3}$ the geometric mean was found to be 49 $\mu g\ m^{-3}$. This was the largest difference found between the two statistics and reflected the extreme peak values typical of this fraction. The same was found to be true of rush hour concentrations which are typically the most erratic of all the fractions monitored, mean values of 59 and 61 $\mu g\ m^{-3}$ and geometric means of 46 and 49 $\mu g\ m^{-3}$ were found for TSP_{AM} and TSP_{PM} respectively.

- Regression analysis found very tight relationships for all winter fractions monitored, this indicated that they originated from the same source. The trends for the all fractions and the rush hour TSP and PM_{10} elevations indicate that this source is traffic. The previous summer regression analysis had shown the same pattern for all PM_X fractions with TSP showing evidence of a strong influence from resuspension which was notably absent in this study.

- Summary statistics showed that summer particulate concentrations were stable throughout weekdays and weekends, with the exception of TSP, which proved to be variable. In contrast, winter weekday mean concentrations of PM_X were found to be in excess of the mean concentrations. Weekend mean concentrations were found to be depressed in comparison to mean concentrations for the whole data set, this being more the case for PM_{10} and $PM_{2.5}$. Rush hour PM_{10} concentrations displayed the reverse trend being elevated at weekends but to a lesser degree. TSP showed similar but more varied trends to PM_X fractions with depressed weekend rush hour concentrations and elevated weekday rush hour concentrations. This, in the light of the large standard errors of the means, was concluded to be the effect individual peak concentrations distorting the statistics.

- The PM_{10} summer/winter ratios (based on mean values) revealed that rush hour PM_{10} concentrations were more elevated in winter than 24 hour PM_{10}, this was concluded to be due to the effects of cold starts in the morning. This being confirmed by the larger morning rush hour TSP elevation compared to the evening rush hour TSP Elevation.

- The importance of using the appropriate statistics for analysis and the need for a full and thorough analysis can not be over stressed. The effect of applying the geometric mean values to the analysis of the winter data has been to temper the initial analysis by mean values.

13. RECOMENDATIONS FOR FURTHER RESEARCH

This work makes some attempt to investigate concentrations of several particulate fractions, their relationships and the changes in these relationships between winter and summer seasons on Archway Road. This is limited by the size and resolution of the data sets and the level of analysis applied to them. Further analysis of the existing data could reveal more information as to:

- The changes in rush hour PM_{10} concentrations and their relationships with TSP rush hour concentrations.
- Daily trends of all particulates and the differences between daily summer and winter patterns.
- The roadside concentrations of PM_{10} in comparison to the site concentrations (which was elevated above the road).
- The influence of canyon effect on the Archway road.
- The inclusion of meteorological and traffic data would be invaluable in the analysis of the trend, especially in the case of TSP and PM_{10} which appear to be most strongly affected.
- The use of TEOM monitors or other suitable 'real time' monitors to provide a higher resolution of data could reveal patterns on an hour to hour basis.
- The use of PM_1 preseperators on such monitors to provide high resolution, long term data sets in more than one location.
- The simultaneous monitoring at a background or rural site to provide direct comparisons.
- The inclusion of cascade impactor data could provide useful insights into changing aerosol distributions throughout the day and throughout the week and week ends.

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